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SOME THEORETICAL AND EXPERIMENTAL ASPECTS OF GAS PHASE E.P.R. SPECTROSCOPY

by

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ABSTRACT

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The derivation of an effective rotational Hamiltonian is discussed. Using these general techniques some spin-dependent interactions in Σ states of quartet and higher multiplicity are cast into operator equivalent form. As a result the two spin-rotation constants required, in principle, for $^4\Sigma$ states are shown to be the same to within experimental error. These results are generalised to cover states of higher multiplicity. A fourth-order spin-spin interaction arising in $^5\Sigma$ states is investigated.

The rotational energy levels of a molecule in a $^2\Pi$ electronic state are described, with particular reference to the OH radical, and some higher order Λ-doubling and hyperfine interactions are cast into operator equivalent form. A comparison is made with effective rotational Hamiltonians used by other workers. A reanalysis of the zero-field Λ-doubling frequencies for OH is outlined. Other higher order interactions appear to be needed to further improve the fit.

The measurement of the gas phase e.p.r. spectrum arising from the $^2\Pi_{3/2}$ $J = 9/2$ rotational levels of OH is detailed and the theory of the g-factors in $^2\Pi$ states is given. Values for molecular g-factors determined from an analysis of e.p.r. measurements on seven rotational levels of OH are quoted, and compared with a pure precession model. Effective g-factors are calculated from these molecular g-factors and compared with published experimental results.

Some initial experiments investigating the possibility of using pyrolysis to generate radicals for gas phase e.p.r. studies are detailed.

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Chapter 6 Radical Production by Pyrolysis

CHAPTER 1

INTRODUCTION

Free radicals are of importance in almost every branch of chemistry, even though most branches are not directly concerned with their study. To understand why these species are of such significance we must consider what is meant by the term 'free radical'. It seems to be a matter of personal preference as to whether a loose or a rigorous definition of a free radical is adopted. The former defines radicals on the grounds of their high reactivity, regardless of their electronic state. Thus the unstable HNO molecule in its ^1A electronic state would be regarded as a radical whereas the stable gasses O_2, NO and NO_2 would not. We shall use the rigorous definition instead. In this case radicals are defined as any species possessing an open-shell electronic state, and hence ^1A HNO would not be regarded as a radical whereas O_2, NO and NO_2 would be classified as such. The majority of species with open-shell electronic states are nevertheless highly unstable with short lifetimes, generally less than one second, and so would still be classified as radicals under the loose definition.

A chemical reaction involves the breaking and/or making of covalent bonds and the redistribution of electrons involved in either of these processes can result in species with open-shell electron configurations. Thus the intermediates in chemical reactions are often free radicals, which is why radicals are of such importance in chemistry. Reactions in solution involving free radical intermediates are similar to those in the gas phase but are further influenced by the presence of the solvent. Since we are not concerned with these complications discussion is restricted to gas phase reactions.

Radicals can undergo various types of reaction, such as decomposition, abstraction and combination, and consequently a wide variety of end products can result. A knowledge of these reaction pathways is important for both kinetic and photochemical studies, although for different reasons - whereas a kineticist determines reaction rates for individual steps involved in the total reaction, a photochemist is concerned with the way in which those intermediates formed in excited states lose their excess energy. Nevertheless, the information provided by such studies is complementary in the sense that both indicate the reaction mechanism. An understanding of the processes involved in these complex gas phase reactions is also essential to those interested in the chemistry of the upper atmosphere and the combustion of fuels.

As a further example of the role played by radicals in gas phase reactions, it has been suggested that many reactions occurring in interstellar gas clouds proceed via free radical intermediates. The evidence for such reactions is supplied by the detection of absorption and emission signals by radioastronomers. The absorption signals arise from the stimulation of absorption by the background radiation. Similarly there are stimulated emission signals. Perhaps more interesting are the so-called maser emission signals which are a consequence of an inverted population of energy levels. The mechanism by which the radicals are formed in an inverted population is not yet fully understood. The interstellar radicals detected so far have been small, such as HCO, OH and CN, but from a knowledge of radical reaction mechanisms we can propose the existence of larger molecules such as hydrocarbons, aldehydes, amines and so on. The genesis and subsequent development of these clouds is likely to be of great astronomical significance.

A rather different aspect of the usefulness of radical studies arises from the possession of open-shell electronic states. This implies the presence of electron spin and/or orbital angular momenta within the molecule, which give rise to interactions not present in a closed-shell molecule. Because the magnetic moments associated with these angular momenta are quite large, the spin-orbit interactions can have a dominating influence on the molecular energy levels. Although this means the analysis of the spectra is more complicated, ultimately far more information about the electronic structure of the molecule can be obtained.

An accurate determination of the parameters describing the intramolecular interactions is invaluable in evaluating theoretical models for the electronic structure: the experimental parameters are compared with those computed using ab initio wavefunctions. The magnetic hyperfine parameters are particularly useful in this respect since they are so sensitive to changes in the distribution of unpaired electrons and hence provide a rigorous test for proposed wavefunctions. Measurements of this order of accuracy call for high resolution experimental techniques such as molecular beam methods, or studies in the microwave and radiofrequency regions. As far as radioastronomers are concerned, the data provided by these high resolution laboratory studies are invaluable in aiding the identification of the source molecule of interstellar signals.

Our particular interest lies in high resolution studies giving information pertaining to the electronic structure of radicals. High resolution studies can be performed on radicals in condensed phases but in this instance there are important, perhaps even dominating environmental effects which can have a marked effect on the spectra. This merely serves to hinder any interpretation in terms of electronic structure and for this reason we are only concerned with gas phase studies. The theoretical work presented in this thesis is concerned with describing certain interactions of angular momenta that arise for molecules in particular electronic states. An understanding of how such interactions arise is essential if the corresponding parameters are to be correlated with electronic structures.

The experiments described here employ the particular high resolution technique of electron paramagnetic resonance (e.p.r.) spectroscopy. If the parameters obtained in these experiments are to be interpreted in terms of molecular wavefunctions it is essential to establish some link between theory and experiment. With this end in mind, we derive an effective Hamiltonian that is restricted so as to operate only within the particular electronic state from which the apectra arise. Each of the terms in this Hamiltonian relates to a different effective interaction of angular momenta. It is of course only possible to distinguish terms with different dependences on the relevant quantum numbers. The parameters in this Hamiltonian are constructed from fundamental molecular quantities, such as bond lengths. Transition frequencies can be predicted using this Hamiltonian, and these can be fitted to the observed spectra by a numerical least squares fitting procedure. These derived parameters thus convey information on the magnitudes of the more fundamental quantities.

In chapter 2 we deal in more detail with the philosophy behind effective Hamiltonians, and with their construction. The derivation of such a Hamiltonian for Σ states of quartet and higher multiplicities is detailed in chapter 3. The remainder of this thesis is concerned more directly with experimental aspects. Chapter 4 describes briefly the technique of e.p.r. spectroscopy and with some practical considerations relevant to radical studies. Chapter 5 is concerned with the detection and analysis of the spectra of the OH radical in its ground $^2\Pi$ electronic state. This analysis requires the construction of an effective Hamiltonian too, and this derivation is outlined. Finally, chapter 6 describes some initial e.p.r. experiments investigating the possibility of generating radicals by pyrolysis.

CHAPTER 2

THE DERIVATION OF AN EFFECTIVE ROTATIONAL HAMILTONIAN

2.1 Introduction

A fundamental prerequisite for the analysis of any spectrum is a model, giving the problem a mathematical framework upon which any calculations can be based and enabling an interpretation of the results to be given, in terms of physically significant quantities. A model in which spectral lines can be correlated with transitions between different quantum mechanical states is the most useful and the most appealing one. In most spectroscopic experiments these states do not evolve with time, i.e. they are stationary states, and so their energies can be obtained from the solution of the time-independent Schrödinger equation

$$H|\psi_i\rangle = E|\psi_i\rangle \qquad (2.1)$$

where H is the total Hamiltonian, the ket $|\psi_i\rangle$ is the i^{th} eigenfunction and the eigenvalue E is the energy of this eigenfunction.

Our interest lies in the spectroscopy of molecules, in which case H will be a molecular Hamiltonian representing the total potential and kinetic energies of the molecule. It is important to understand the nature of the molecular eigenfunction $|\psi_i\rangle$, a function of both nuclear and electronic coordinates, which we shall represent by Q and x respectively. Due to the relative orders of magnitude associated with electronic, vibrational and rotational motions a factorisation of a wavefunction, $\phi(x;Q)$, into two functions, one dependent on electronic coordinates only and one on nuclear coordinates only, would be convenient:

$$\phi(x;Q) = \rho(x)\,\chi(Q) \qquad (2.2)$$

The aim of the Born and Oppenheimer Separation (1) is to effect such a separation of electronic, vibrational and rotational motions. To achieve this, the functions and operators involved are expanded as a power series in ζ, the relative nuclear displacements from the equilibrium nuclear configuration, with an order parameter K, defined as

$$K = \left(\frac{m}{M_n}\right)^{\frac{1}{4}} \qquad (2.3)$$

where m is the mass of the electron and M_n the reduced mass of the nuclei. As a result of using this expansion parameter the electronic energies are of order K^0, the vibrational energies are of order K^2 and the rotational energies are of order K^4. To order K^2 it is indeed possible to separate the wavefunctions into products of electronic and nuclear functions but this is not possible for higher orders in the expansion, without making approximations.

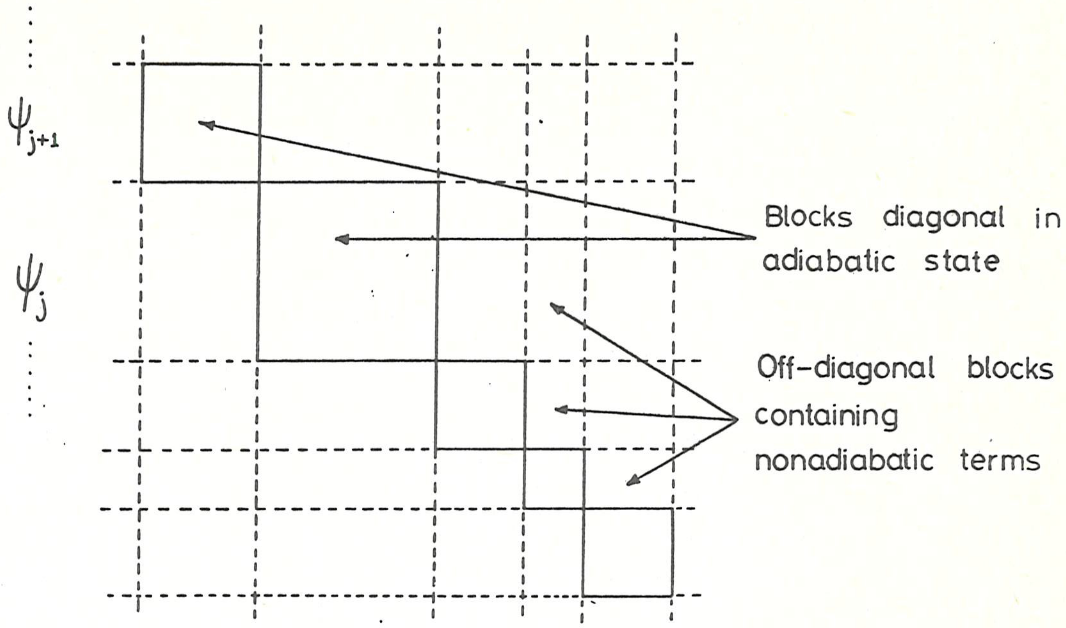
Consider the adiabatic approximation, which arises in fourth order of this expansion. In this approximation the electrons are assumed to follow the nuclei adiabatically, or, in other words, there is no change in electronic state as the nuclei move, and as a consequence the electronic and nuclear coordinates can be separated. We shall refer to such states, $|\phi\rangle$, as 'Born-Oppenheimer' states or 'adiabatic' states. Terms occur in higher orders of this expansion which represent mixing of different adiabatic states; such terms are referred to as nonadiabatic terms and their origin is often ascribed to the breakdown of the Born-Oppenheimer Approximation. The true molecular eigenfunctions $|\psi_i\rangle$ are thus linear combinations of these adiabatic states

$$|\psi_i\rangle = \sum_j c_{ij} |\phi_j\rangle \qquad (2.4)$$

However each molecular eigenfunction $|\psi_i\rangle$ will generally have a dominant contribution from a particular adiabatic state and so it is still permissible to refer to this state in terms of the dominant adiabatic wavefunction.

The analysis of molecular spectra using the true molecular eigenfunctions is impracticable since to include the effects of all these nonadiabatic terms a matrix diagonalisation of an infinite matrix would have to be performed. Even if this matrix were to be suitably truncated the problem would still be very difficult to handle. Ideally a matrix representation is required that contains no terms off-diagonal in electronic state, in which case the matrix representation is still an infinite array but consists only of submatrices, each only containing elements pertaining to a single adiabatic state. Eigenvalues can be obtained from each of these diagonal blocks, from which it is possible to determine the transition frequencies. The Hamiltonian which would give such a matrix representation we refer to as a 'spectroscopically useful' Hamiltonian, and its derivation will involve artificially reducing to a negligible level the effects of all elements off-diagonal in electronic state. This is illustrated in figure 1. In practice we use an effective Hamiltonian that only operates within the manifold of a particular adiabatic state and there are three methods

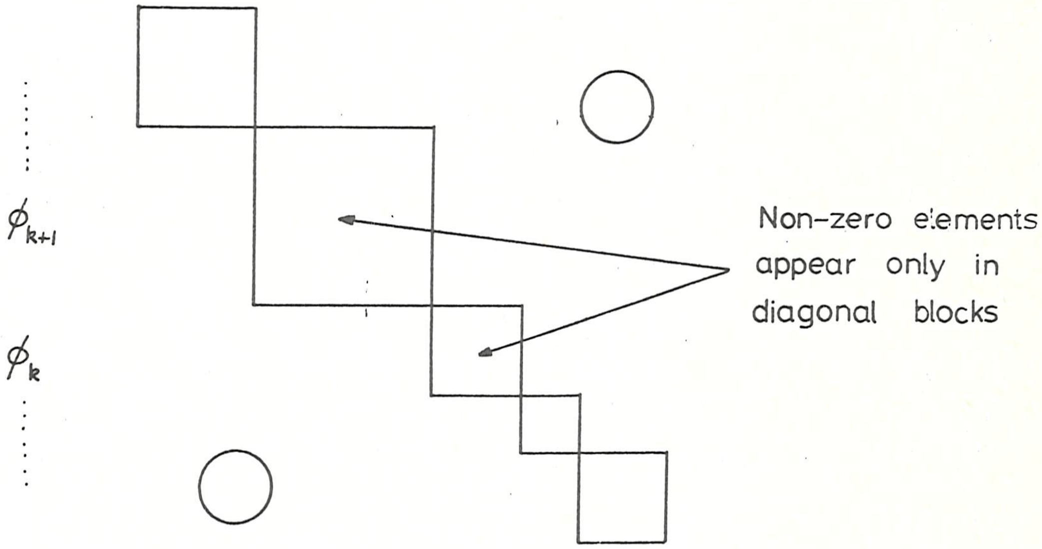
Figure 1



Blocks diagonal in adiabatic state

Off-diagonal blocks containing nonadiabatic terms

i. Matrix representation of the total Hamiltonian.
Basis states are linear combinations
of adiabatic states.



Non-zero elements appear only in diagonal blocks

ii. Matrix representation of a spectroscopically
useful Hamiltonian.
Basis states are adiabatic states.

commonly used for its derivation, namely the contact transformation (2), the Van Vleck transformation (3) and degenerate perturbation theory (4).

The first two of these methods involve the application of a unitary transformation to the wavefunctions, the latter being a slightly more specific version of the former. The contact transformation has proved particularly useful for dealing with vibration-rotation interaction. The Van Vleck transformation involves the use of perturbation theory type expressions and the form of the resulting effective Hamiltonian can be shown to be identical to that obtained by degenerate perturbation theory for terms up to third order (5). The technique of degenerate perturbation theory is the one used most extensively in subsequent chapters and so will be outlined in more detail in the following section.

It is perhaps worthwhile noting at this stage that the consideration of these nonadiabatic terms is of particular importance in the discussion of rotational levels for two reasons. Firstly the rotational energies first appear in order K^4 of the expansion and so the moment higher order rotational interactions are considered then nonadiabatic terms, which, as has been mentioned, appear in orders $> K^4$, will manifest themselves, especially as they can be of much the same magnitude as the rotational terms of order K^4. Secondly, precise measurements of rotational transitions can be made in the microwave region and so such effects can readily be detected.

2.2 Degenerate Perturbation Theory

In this section we shall outline the technique of degenerate perturbation theory. Messiah (4) has described this, using the methods of both Bloch (6) and Kato (7). A rather more readable account of the derivation of an effective Hamiltonian has been given by Soliverez (8), using the formalism set up by Bloch (6).

The eigenfunctions $|\psi_i\rangle$ of the total Hamiltonian, which operates over all vector space, form a complete orthonormal set. We want a Hamiltonian that operates only within a particular manifold of the total Hilbert space. In other words we wish to project the effects of the total Hamiltonian operator onto a chosen vector space which is of dimension less than that of the total vector space, and hence to construct an effective Hamiltonian that operates only within this chosen vector space and with the equivalent operator form within this manifold of the total Hamiltonian. The geometrical interpretation of this projection process is far more readily appreciated for a total vector space of only two or three dimensions.

The operator which brings about this projection of the total Hamiltonian is a projection operator, P_0.

Sŏliverez (8) shows that it is possible to set up an effective Hamiltonian which has the following properties:

1) It operates only within a manifold of dimension less than that of the total vector space.

2) Its eigenvalues are identical to those corresponding eigenvalues of the total Hamiltonian.

3) Its eigenvectors are related in some simple manner to those of the total Hamiltonian.

4) It can be expanded as a power series in terms of a perturbation V, and is Hermitian to all orders of the expansion.

We shall indicate briefly here how such a Hamiltonian is set up.

The total Hamiltonian is split into two parts

$$H = H_0 + V \qquad (2.5)$$

where the eigenvalues and eigenvectors of H_0 are known:

$$H_0 |\psi_j\rangle_0 = E_j |\psi_j\rangle_0 \qquad (2.6)$$

where the eigenfunctions $|\psi_j\rangle_0$ form a complete orthonormal set over all vector space.

V is a perturbation to this Hamiltonian and we are interested in its effects on the eigenvectors and eigenvalues of H_0. In particular, we want to concern ourselves with the eigenvectors spanning the particular manifold onto which the total Hamiltonian is projected; these will have a particular eigenvalue, E_0. The projection operator is defined as

$$P_0 = \sum_k | k\rangle\langle k | \qquad (2.7)$$

where the $|k\rangle$ are the eigenvectors spanning the manifold under consideration. P_0 must commute with the Hamiltonian and so we have

$$H_0P_0 = P_0H_0 = E_0P_0 \qquad (2.8)$$

The eigenvalue E_0 is in general degenerate, and the effect of the perturbation V is to lift this degeneracy. The eigenvalues of the perturbed energy levels are given by

$$(H_0 + V)|\psi_i\rangle = (E_0 + \Delta_i)|\psi_i\rangle$$

which can be rearranged to give

$$(H_0 - E_0)|\Psi_i\rangle = (\Delta_i - V)|\Psi_i\rangle \tag{2.9}$$

Δ_i are the shifts in the energy levels due to the perturbation V. Using (2.8) it can easily be shown that

$$P_0 V|\Psi_i\rangle = \Delta_i P_0|\Psi_i\rangle = \Delta_i|\Psi_i\rangle_0 \tag{2.10}$$

where $|\Psi_i\rangle_0$ are eigenfunctions of H_0, and in particular are those eigenfunctions $|k\rangle$ spanning the vector space under consideration.

There is a complementary projection operator Q_0 which follows from the closure relationship:

$$\begin{aligned} Q_0 &= 1 - P_0 \\ &= \sum_l |l\rangle\langle l| \end{aligned} \tag{2.11}$$

where $|l\rangle$ are the eigenvectors that have been excluded from equation (2.7) since they do not span the manifold we are interested in. Q_0 also has the property

$$Q_0 = \left(\frac{Q_0}{a}\right)(H_0 - E_0) = (H_0 - E_0)\left(\frac{Q_0}{a}\right) \tag{2.12}$$

where

$$\left(\frac{Q_0}{a^n}\right) = \sum_l \frac{|l\rangle\langle l|}{(E_l - E_0)^n} \tag{2.13}$$

From equations (2.9) and (2.12) it follows that

$$Q_0|\Psi_i\rangle = \left(\frac{Q_0}{a}\right)(\Delta_i - V)|\Psi_i\rangle \tag{2.14}$$

We are now able to find a relationship for $|\Psi_i\rangle$ in terms of the unperturbed eigenvectors $|\Psi_i\rangle_0$:

$$\begin{aligned} |\Psi_i\rangle &= (P_0 + Q_0)|\Psi_i\rangle \\ &= |\Psi_i\rangle_0 + \left(\frac{Q_0}{a}\right)(\Delta_i - V)|\Psi_i\rangle \end{aligned} \tag{2.15}$$

The Δ_i terms can be eliminated from (2.15) by repeated use of equation (2.10) to give an expansion of $|\Psi_i\rangle$ in terms of $|\Psi_i\rangle_0$, V, P_0 and

(Q_0/a). The eigenvectors for the perturbed and unperturbed Hamiltonians are thus related by an identity of general form

$$|\psi_i\rangle = U|\psi_i\rangle_0 \tag{2.16}$$

where U is an operator involving V, P_0 and (Q_0/a) and can be expanded as an infinite series in terms of these operators. Substitution of (2.16) into (2.10) leads to the following eigenvalue expression

$$P_0VU|\psi_i\rangle_0 = \Delta_i|\psi_i\rangle_0 \tag{2.17}$$

If we identify (P_0VU) with the effective Hamiltonian we can see that it does indeed possess the properties listed by Soliverez (8), although its hermiticity has not been demonstrated. Note that Δ_i denote the energy shifts about an origin E_0. Equation (2.17) is also particularly convenient in that it uses eigenfunctions of the unperturbed Hamiltonian as basis functions, and these are by definition known.

We are now in a position to be more specific in our derivation of an effective molecular Hamiltonian. As has been discussed in the previous section, it is prudent to use adiabatic electronic wavefunctions as the basis states since this greatly simplifies the calculation of the molecular energy levels. The basis functions $|\psi_i\rangle_0$ are thus taken to be the adiabatic electronic states that are of interest, and so H_0 will be the Hamiltonian of which such electronic states are eigenvalues. The effects of the nonadiabatic terms, such as spin-orbit coupling and L-uncoupling terms, that cause mixing of the adiabatic states, can be included by treating these terms as a perturbation, V. In practice since the adiabatic states do not by definition change as the nuclei move, the perturbation V will also contain the terms of order K^2 and K^4 that describe the vibrational and rotational motions of the nuclei. We are not concerned at this stage with the vibrational motions of the nuclei and we can avoid dealing with them by redefining our basis states so as to be vibronic states of the molecule, $|\psi_i; v\rangle_0$; these would be adiabatic in the sense that there would be no change in the vibronic state as the nuclei rotate. In order to apply degenerate perturbation theory, the Hamiltonian describing these states is assumed to have been solved:

$$H_0|\psi_i; v\rangle_0 = E_{iv}|\psi_i; v\rangle_0 \tag{2.18}$$

We shall suppress the vibrational quantum number v, its presence being taken as understood. The effects of nuclear spin will be ignored throughout this chapter.

Miller (9) has shown how to derive an effective rotational Hamiltonian for a molecule in a particular electronic state, which operates only within the rotational subspace of that state. He partitions the total Hamiltonian as follows

$$H = H_0 + \lambda V \qquad (2.19)$$

where H_0 and V have the significance discussed above; λ is a dimensionless parameter taking values between 0 and 1 that denotes the order of the perturbation expansion.

The projection operators P_0 and Q_0 are given the more explicit definitions

$$\begin{aligned} P_0 &= \sum_{k} | l_0 k \rangle \langle l_0 k | \\ \frac{Q_0}{a^n} &= \sum_{l \neq l_0} \sum_{k} \frac{| lk \rangle \langle lk |}{(E_{l_0} - E_l)^n} \end{aligned} \qquad (2.20)$$

where l_0 refers to the adiabatic state of interest,

l refers to adiabatic states other than l_0,

k refers to the rotational quantum numbers.

The effective rotational Hamiltonian is given by

$$H_{eff} = \lambda P_0 V U \qquad (2.21)$$

As has already been noted, U can be expanded as an infinite series

$$U = \sum_{n=0}^{\infty} \lambda^n U^n \qquad (2.22)$$

where U^n is given by the general formula

$$U^n = \sum_{n}^{\dagger} S^{K_1} V S^{K_2} V \ldots S^{K_n} V P_0$$

except that $\quad U^0 = P_0 \qquad (2.23)$

K_n can take the values 0, 1, 2 . . .

such that $\quad K_1 + K_2 + \ldots + K_n = n$

$$K_1 + K_2 + \ldots + K_j \geqslant j \quad (j = 1,2 \ldots, n-1)$$

and where

$$S^0 = -P_0$$

$$S^n = (Q_0/a^n) \text{ for } n \neq 0$$

Note that both Miller (9) and Messiah (4) leave U^0 undefined. As noted by Freed (10), certain terms in the expansion are in fact non-Hermitian but by taking the Hermitian average of such terms the effective Hamiltonian becomes Hermitian to all orders. Equation (2.21) can thus be expanded as follows.

By use of equations (2.22) and (2.23):

$$\begin{aligned} H_{eff} &= P_0 VU \\ &= \lambda P_0 V P^0 \\ &\quad + \lambda^2 \left\{ P_0 V (Q_0/a) V P_0 \right\} \\ &\quad + \lambda^3 \left\{ P_0 V (Q_0/a) V (Q_0/a) V P_0 - \left[P_0 V (Q_0/a^2) V P_0 V P_0 \right]^{\dagger} \right\} \\ &\quad + \lambda^4 \left\{ P_0 V (Q_0/a) V (Q_0/a) V (Q_0/a) V P_0 \right. \\ &\qquad - P_0 V (Q_0/a^2) V P_0 V (Q_0/a) V P_0 \\ &\qquad - \left[P_0 V (Q_0/a^2) V (Q_0/a) V P_0 V P_0 \right]^{\dagger} \\ &\qquad \left. + \left[P_0 V (Q_0/a^3) V P_0 V P_0 V P_0 \right]^{\dagger} \right\} \\ &\quad + \lambda^5 \ldots \end{aligned} \qquad (2.24)$$

where the square brackets marked by a dagger mean that the Hermitian average of the enclosed terms are also needed. The term in parentheses after λ^n represents the n^{th} order contribution to the effective Hamiltonian. The number of terms involved can be seen to increase rapidly as the perturbation treatment is taken to increasingly higher order. Even a fourth order treatment is very tedious and complicated, and higher orders than this become impracticable. However the expansion of the effective Hamiltonian is expected to converge fairly rapidly, although the rate of convergence will depend to some extent on the manner in which the Hamiltonian is originally partitioned. In practice the total Hamiltonian is partitioned in such a way that the dominant interactions arise in first order of perturbation theory. Smaller interactions are included in the effective Hamiltonian by appealing to higher orders until the required precision of the eigenvalues, a limit usually imposed by experiment, is reached. If higher order terms than say fourth need to be calculated before such conditions are reached, or in other words, if convergence is slow, then an unsuitable partitioning of the Hamiltonian has probably been used. For most spectroscopic applications, calculations of higher order than fourth are thankfully unnecessary.

Equation (2.24) is rather abstract and it is still not obvious from its form how the explicit operator form of the effective Hamiltonian arises. In the next section we shall deal briefly with angular momentum operators and some standard spherical tensor techniques, after which we shall be in a position to give an illustrative calculation, showing how from equation (2.24) it is possible to derive an effective Hamiltonian written in terms of operator equivalents.

2.3 Angular Momenta and Spherical Tensors

It is not intended to give a thorough account of angular momenta and spherical tensor theory in this section, the aim is merely to give a few of the basic ideas and to indicate some useful relations that will be called upon in subsequent calculations. There are several basic texts on these subjects, for instance, Edmonds (11), Brink and Satchler (12) and Rose (13), although it should be noted that the phase conventions observed by these authors differ. We follow the phase conventions given by Rose.

Angular Momenta

Angular momentum operators can be defined as those momentum operators that obey the commutation rules $\left[p_x, p_y\right] = ip_z$ and cyclic permutations of x, y, z, where p_x, p_y, p_z are components of the angular momentum operator $\underline{p}$. Note that since these components do not commute, then it is not possible to determine them all simultaneously. However since the angular momentum and the energy are both constants of motion then the angular momentum operator does commute with the Hamiltonian and so these operators must possess at least one common basis function. This is a pertinent point as in order to calculate matrix elements of the Hamiltonian operator well-defined basis functions are needed. Due to the ease of use of commutation rules and to the need to find these basis functions, it is convenient to write the Hamiltonian operator in terms of angular momentum operators and their components rather than in terms of differential operators. The basis functions then obtained are defined in terms of quantum numbers relevant to the individual angular momenta. The physical significance of angular momenta within an atomic or molecular system is easily appreciated in terms of a precession model. The Larmor precession of the nuclear spin angular momentum about the direction of an applied magnetic field is well known, for example. In a molecular system the axes of precession might be internal axes, such as the internuclear axis of a linear molecule, or an external axis determined by the direction of an applied electric or magnetic field.

It can be shown that the components of angular momentum operators generate infinitesimal rotations about their corresponding axes and consequently the Hamiltonian has to be invariant to rotation about those axes (i.e. angular momentum is conserved about that axis).

Consider the various angular momenta that can arise in a molecule. Firstly there is the electronic orbital angular momentum $\underline{L}$ which is the sum of the orbital angular momenta of each of the electrons

$$\underline{L} = \sum_i \underline{l}_i = \sum_i \underline{r}_i \times \underline{p}_i \qquad (2.25)$$

where $\underline{r}_i$ and $\underline{p}_i$ are respectively the position and momentum operators for the individual electrons. $\underline{L}^2$ commutes with L_z and so these operators must have a common basis; these eigenfunctions can be shown to be spherical harmonics. $\underline{G}$ is the angular momentum due to vibration of the nuclei, but as only diatomics are being dealt with here this operator will not be considered. $\underline{S}$ and $\underline{I}$ are the electronic spin and nuclear spin angular momenta respectively while finally there is $\underline{R}$, the angular momentum due to rotation of the nuclei. It is possible to couple these angular momenta together, and hence we have

$$\begin{aligned} \underline{J} &= \underline{R} + \underline{L} + \underline{S} \\ \underline{F} &= \underline{J} + \underline{I} \end{aligned} \qquad (2.26)$$

$\underline{J}$ is the total angular momentum in the absence of nuclear spins, while $\underline{F}$ is the grand total angular momentum. Conservation of angular momentum applies to the total angular momentum ($\underline{F}$ or $\underline{J}$) but not necessarily to the component angular momenta. This is equivalent to saying that only the conserved angular momenta possess well defined eigenfunctions. In general for any conserved angular momentum $\underline{P}$ we have the well known relations

$$\begin{aligned} \underline{P}^2 \left| P\, m_P \right\rangle &= P(P+1) \left| P\, m_P \right\rangle \\ P_z \left| P\, m_P \right\rangle &= m_P \left| P\, m_P \right\rangle \end{aligned} \qquad (2.27)$$

P is the quantum number of the angular momentum $\underline{P}$ and can take integral or half-integral non-negative values. m_P is the quantum number relating to the projection of the operator $\underline{P}$ along the z axis (as yet undefined) and takes the (2P + 1) values P, P - 1, . . ., - P. The eigenfunctions $|P\ m_P\rangle$ are completely defined in terms of the quantum numbers P and m_P. The possibility of different coupling schemes and the different sets of well-defined quantum numbers that emerge will be dealt with in the next section.

By successive infinitesimal rotations about an axis it is possible to generate an operator for rotation through a finite angle α about, say, the z axis. This operator is D_α defined as

$$D_\alpha = 1 - \frac{i\alpha}{\hbar} P_z - \frac{\alpha^2}{4\hbar^2} P_z^2 + \ldots = \exp\left(-i\alpha P_z/\hbar\right) \qquad (2.28)$$

or in general, for a rotation of a physical system in which the coordinates of points after rotation are related to the original coordinates by the Euler angles α, β, γ

$$D(\alpha,\beta,\gamma) = \exp(-i\alpha P_z/\hbar)\exp(-i\beta P_y/\hbar)\exp(-i\gamma P_z/\hbar) \qquad (2.29)$$

The matrix elements of this rotation operator are defined as

$$\langle P\ m_P |\ D(\alpha,\beta,\gamma)\ | P\ m_P'\rangle = \mathcal{D}^{(P)}_{m_P m_P'}(\alpha,\beta,\gamma) \qquad (2.30)$$

The properties of these rotation matrix elements are given in, for instance, the above-mentioned texts. It can be shown that the $\mathcal{D}^{(P)}_{m_P m_P'}(\alpha,\beta,\gamma)$ are eigenfunctions of the angular momentum operators. For instance, the spherical harmonics, which are eigenfunctions of $\underline{L}^2$ and L_z, are in fact specialised rotation matrix elements with P = integer and $m_P = m_P' = 0$. The angular momentum eigenfunctions $|P\ m_P\rangle$ in general can be defined in terms of rotation matrix elements.

Spherical Tensors

An irreducible spherical tensor operator is written in the form

$$T^k_q(\underline{P})$$

where k = 0, 1, 2, . . ., is the rank of the tensor, and there are (2k + 1) components labelled q, where q = k, k - 1, . . ., - k.

It is possible to link spherical tensor theory with that of angular momentum commutation relations. For instance, if k = 1 then the $T^1_q(\underline{P})$ are related to the components of a vector $\underline{P}$ (a vector is a first rank tensor)

$$\begin{aligned} T^1_{\pm 1}(\underline{P}) &= \mp\frac{1}{2}\,(P_x \pm iP_y) \\ T^1_0(\underline{P}) &= P_z \end{aligned} \qquad (2.31)$$

Angular momentum operators are vectors, and can therefore be written in spherical tensor form. Tensor operators of rank 2 or more can also arise in the Hamiltonian operator; for instance, the dipolar spin-spin interaction operator and the electric quadrupole operator are both second rank tensors. The trivial zeroth rank tensor is a scalar quantity, i.e. a constant term, in the sense of being independent of quantum numbers. In addition the spherical harmonics (in a modified form) are basic examples of spherical tensors.

We therefore choose to write all the terms in the Hamiltonian operator in spherical tensor notation, since we are then able to use the extremely useful, and powerful, spherical tensor techniques in the calculation of matrix elements. Products of spherical tensor operations can be treated without much difficulty, which is of particular relevance when products of matrix elements are to be written in an equivalent operator form. Particular relations that will be of importance are as follows; these, and other standard expressions, can be found in aforementioned texts on angular momentum -

Tensor product of two tensor operators -

$$T^k_q(\underline{A}, \underline{B}) = (2k+1)^{\frac{1}{2}} \sum_{q_1} \sum_{q_2} T^{k_1}_{q_1}(\underline{A})\, T^{k_2}_{q_2}(\underline{B})\, (-1)^{k+2k_1-q} \begin{pmatrix} k_1 & k_2 & k \\ -q_1 & -q_2 & q \end{pmatrix} \qquad (2.32)$$

with $|k_1 - k_2| \leqslant k \leqslant |k_1 + k_2|$

Scalar product of two tensor operators -

$$T^k(\underline{A}).\,T^k(\underline{B}) = \sum_q (-1)^q\, \underline{T}^k_q(\underline{A})\, \underline{T}^k_q(\underline{B}) \qquad (2.33)$$

Wigner-Eckart theorem -

$$\langle P\ m_P |\ T^k_q\ (\underline{P})\ | P'\ m'_P \rangle = (-1)^{P-m_P} \begin{pmatrix} P & 1 & P' \\ -m_P & q & m'_P \end{pmatrix} \langle P \| T^k\ (\underline{P}) \| P' \rangle \tag{2.34}$$

Relation between tensor operators in different coordinate systems - these systems can be transformed into each other by means of rotations through the Euler angles. Let p and q be the components of the tensor in the two different coordinate systems.

$$T^k_p\ (\underline{A}) = \sum_q \mathcal{D}^{(k)*}_{pq}(\alpha, \beta, \gamma)\ T^k_q\ (\underline{A}) \tag{2.35}$$

where the asterisk indicates the complex conjugate of the rotation matrix.

The symbol $\langle P \| T^k\ (\underline{P}) \| P' \rangle$ in equation (2.34) is a reduced matrix element, and is a matrix element that contains no reference to a coordinate system. The Wigner-Eckart theorem enables terms dependent on the orientation of the coordinate system, mainly terms involving m_P, to be factored off. The symbol $\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix}$ in equations (2.32) and (2.34) is a Wigner 3-j symbol, which is a coefficient relating the eigenvectors corresponding to the angular momenta $\underline{j}_1$ and $\underline{j}_2$ to those corresponding to the angular momentum $\underline{j}_3$ that results from coupling $\underline{j}_1$ with $\underline{j}_2$ -

$$|\ j_1\ j_2\ j_3\ m_3 \rangle = \sum_{m_1} \sum_{m_2} |\ j_1\ m_1 \rangle |\ j_2\ m_2 \rangle\ (-1)^{j_1 - j_2 - m_3}\ (2j_3+1)^{\frac{1}{2}} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & -m_3 \end{pmatrix} \tag{2.36}$$

Wigner 3-j symbols are simply related to Clebsch-Gordan coefficients - they have the same significance. Wigner symbols are used here because they have greater symmetry than the corresponding Clebsch-Gordan coefficients and they are easier to manipulate.

The symmetry properties of Wigner symbols are given in the standard texts. Only those that will be recalled later will be given here. First note that the 3-j symbol $\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix}$ is zero unless j_1, j_2, j_3 satisfy the triangle rule

$$|j_1 - j_2| \leqslant j_3 \leqslant (j_1 + j_2) \tag{2.37}$$

and m_1, m_2, m_3 obey the sum rule

$$m_1 + m_2 + m_3 = 0 \qquad (2.38)$$

The only other relations of particular relevance in subsequent calculations are those by which 3-j (and 6-j) symbols can be reexpressed in terms of Wigner 6-j symbols; for instance a product of two 3-j symbols can be contracted in the following manner -

$$\begin{pmatrix} j_1 & l_2 & l_3 \\ m_1 & \mu_2 & -\mu_3 \end{pmatrix}\begin{pmatrix} l_1 & j_2 & l_3 \\ -\mu_1 & m_2 & \mu_3 \end{pmatrix} = (-1)^p \sum_{j_3} (2j_3+1) \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix}\begin{pmatrix} l_1 & l_2 & l_3 \\ \mu_1 & -\mu_2 & m_3 \end{pmatrix}\begin{Bmatrix} j_1 & j_2 & j_3 \\ l_1 & l_2 & l_3 \end{Bmatrix} \qquad (2.39)$$

where $p = l_1 + l_2 + l_3 + \mu_1 + \mu_2 + \mu_3$

and $\begin{Bmatrix} j_1 & j_2 & j_3 \\ l_1 & l_2 & l_3 \end{Bmatrix}$ is a Wigner 6-j symbol, which is a coefficient arising from coupling of three angular momenta.

Similarly, by use of the Biedenharn-Elliot relationship, a pair of 6-j symbols can be rewritten -

$$\begin{Bmatrix} j_1 & j_2 & j_{12} \\ j_3 & j_{123} & j_{23} \end{Bmatrix}\begin{Bmatrix} j_{23} & j_1 & j_{123} \\ j_4 & j & j_{14} \end{Bmatrix} = \sum_{j_{124}} (-1)^s \quad (2j_{124}+1) \begin{Bmatrix} j_3 & j_2 & j_{23} \\ j_{14} & j & j_{124} \end{Bmatrix}$$

$$\times \begin{Bmatrix} j_2 & j_1 & j_{12} \\ j_4 & j_{124} & j_{14} \end{Bmatrix}\begin{Bmatrix} j_3 & j_{12} & j_{123} \\ j_4 & j & j_{124} \end{Bmatrix} \qquad (2.40)$$

where $s = j_1 + j_2 + j_3 + j_4 + j_{12} + j_{23} + j_{14} + j_{123} + j + j_{124}$

In the next section the second order effective rotational Hamiltonian for a linear molecule in a Σ state of general multiplicity will be derived, in order to illustrate how the above relations can be used to reduce the perturbation expressions to an effective operator form.

2.4 Second Order Effective Rotational Hamiltonian for a Linear Molecule in a Σ State

The derivation of this Hamiltonian and its reduction to operator equivalents are performed along similar lines to those described by Miller (9). The total Hamiltonian is partitioned as in equation (2.19)

$$H = H_0 + \lambda V$$

H_0 contains terms that give the energy of the adiabatic state, and also terms describing the vibrational energy. V contains rotational and spin dependent terms, nonadiabatic interactions being included amongst them. V is taken to be

$$V = H_{ROT} + H_{SO} + H_{SR} + H_{SS} \qquad (2.41)$$

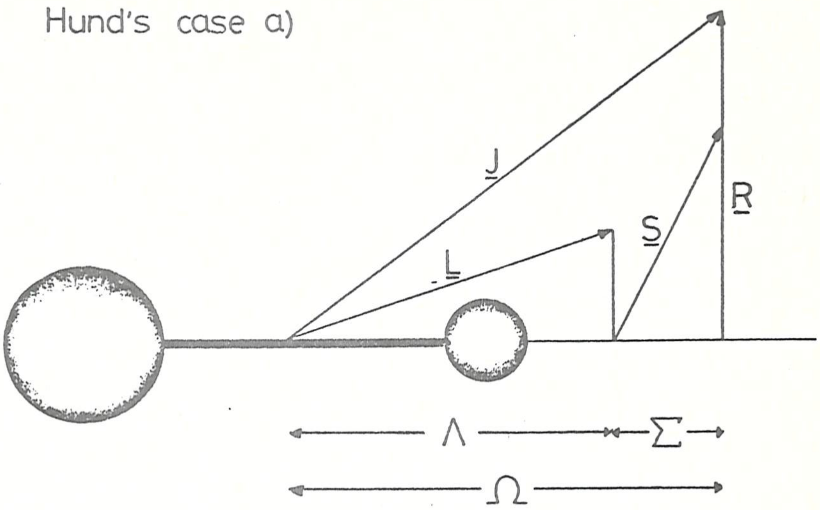
where the effects of nuclear spin have been ignored.

H_{ROT} is the nuclear rotational Hamiltonian
H_{SO} represents the spin-orbit interaction
H_{SR} is the spin-rotation Hamiltonian
H_{SS} represents the spin-spin interaction

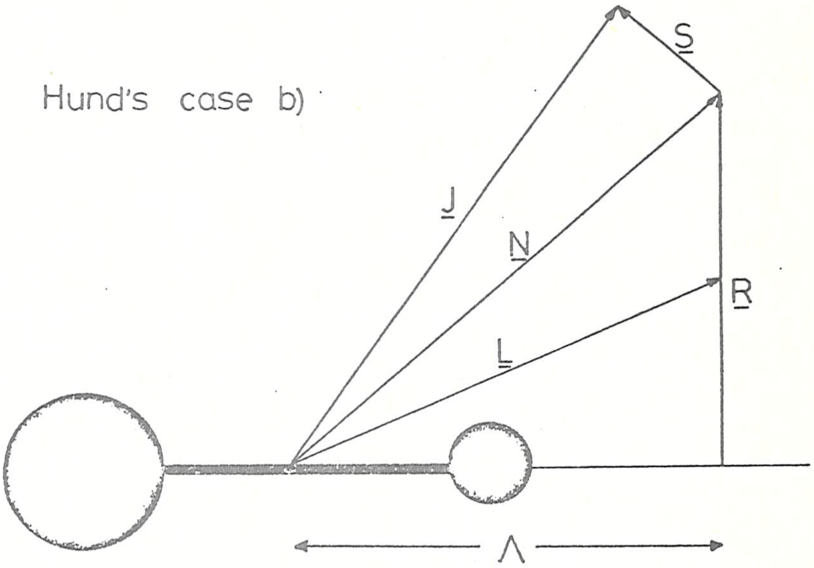
Since the effects of the last two terms in (2.41) are usually very much smaller than those of the first two then the accuracy of the effective Hamiltonian is not significantly altered by including only the first order effects of these latter terms. This does not mean that the effective Hamiltonian neglects certain terms, since 2nd or higher order terms involving H_{SR} and H_{SS} have exactly the same operator dependence as 3rd or higher order terms of H_{ROT} and H_{SO} and are likely to be of similar magnitude. The higher order effects of H_{SS} and H_{SR} are thus contained in the parameters describing higher order effects of H_{SO} and H_{ROT}. This does make interpretation of the parameters difficult however.

The basis functions for this calculation have to be eigenfunctions of H_0, as already mentioned. No reference is made however to interactions involving the electron spin and so these basis functions are not uniquely defined. We therefore have a certain degree of choice in deciding on the spin basis functions. The set of quantum numbers that completely define the molecular wavefunctions is determined by the manner in which the various angular momenta are coupled. Hund (14) investigated the various coupling schemes that can arise and showed that there are five possibilities, now known as Hund's coupling cases a) to e). Diatomic molecules are described adequately by either case a) or case b), although case c) is of occasional value.

Figure 2 illustrates coupling schemes a) and b). Case a) is of value when the spin-orbit interaction is quite large (relative to the rotational interaction). The orbital angular momentum $\underline{L}$ precesses about the internuclear axis. L_z, the projection of $\underline{L}$ onto the internuclear axis, remains a constant of the motion but $\underline{L}$ itself is not conserved. The quantum number $\Lambda = |m_L| = 0, 1, 2, \ldots$ can be used to classify the states. $\underline{S}$ is coupled strongly to $\underline{L}$ by the spin-orbit interaction. The quantum number m_S is then equivalent to Σ, which relates to the projection of $\underline{S}$ along the



Hund's case a)



Hund's case b)

Figure 2 Vector coupling diagrams for Hund's cases a) and b).

internuclear axis. $\underline{L}$ and $\underline{S}$ are coupled with the angular momentum $\underline{R}$ to produce the total angular momentum $\underline{J}$ -

$$\underline{J} = \underline{R} + \underline{L} + \underline{S}$$

The quantum number relating to the projection of $\underline{J}$ along the molecular axis is Ω, and is given by

$$\Omega = \Lambda + \Sigma \qquad (2.42)$$

If an external electric or magnetic field is applied then an additional quantum number relating to the projection of $\underline{J}$ onto the imposed z axis is needed, which is labelled m_J. External fields will not be considered in this example, but m_J is included for the sake of completeness.

The basis set in this case is completely defined in terms of the above mentioned quantum numbers:

$$|\eta\,\Lambda;\,S\,\Sigma;\,J\,\Omega\,m_J\rangle$$

η is a label distinguishing between electronic states possessing the same S and Λ values.

The case b) scheme is important when spin-orbit coupling is small, so that $\underline{S}$ is not coupled to the internuclear axis. $\underline{L}$ has the same significance as for case a). In case b) it is coupled with $\underline{R}$ to form $\underline{N}$, the total angular momentum apart from spin

$$\underline{N} = \underline{R} + \underline{L}$$

This is then coupled with $\underline{S}$ to form the total angular momentum $\underline{J}$

$$\underline{J} = \underline{N} + \underline{S}$$

The quantum numbers Ω and Σ are undefined in this scheme, although a quantum number K, which relates to the projection of $\underline{N}$ onto the internuclear axis, is needed. The basis set for case b) takes the form

$$|\eta\,\Lambda;\,S\,N\,K\,J\,m_J\rangle$$

Case c) describes the situation that arises when the spin-orbit coupling is stronger than the coupling to the internuclear axis. $\underline{L}$ and $\underline{S}$ in this case form a resultant $\underline{J}_a$ which precesses about the molecular axis. $\underline{J}$ is then the resultant of coupling $\underline{J}_a$ with $\underline{R}$. In this case the quantum numbers Λ and Σ lose all significance, although Ω remains a good quantum number.

In this calculation a basis set conforming to Hund's case a) is chosen. In one sense, a molecule in a Σ state cannot conform to a case a) coupling scheme as there is no first order spin-orbit coupling. However, a second order spin-orbit coupling can arise from the admixture of other electronic states, hence leading to a coupling of $\underline{S}$ to the molecular axis. The quantum numbers Σ and Ω remain well-defined. This situation has been recognised by Kopp and Hougen (15) who termed this a case a)' coupling scheme. Tatum and Watson (16) however prefer to modify the definition of a case a) scheme to one which covers both of the above possibilities. The required alteration is merely to define the case a) scheme as one in which Ω and Σ are good quantum numbers.

The first order effective Hamiltonian is readily derived from equations (2.24) and (2.41) by setting L = 0

$$H^{(1)}_{eff} = (P_0 VU)_{(1)}$$

$$= BT^1(\underline{J}-\underline{S})\cdot T^1(\underline{J}-\underline{S}) + \gamma\, T^1(\underline{J}-\underline{S})\cdot T^1(\underline{S}) + \tfrac{2}{3}\sqrt{6}\,\lambda\, T^2_{q=0}(\underline{S},\underline{S}) \qquad (2.43)$$

with the usual linear molecule restriction (given specifically for Σ states)

$$T^1_{q=0}(\underline{J}-\underline{S}) \equiv J_z - S_z = 0 \qquad (2.44)$$

B in equation (2.43) is the rotational constant, γ is the spin-rotation constant and λ the dipolar spin-spin interaction constant. The component q in the spherical tensors refers to the projection of angular momenta onto the internuclear frame, i.e. in a molecule-fixed coordinate system. The label p will be used for components in a space-fixed axis system. The $\frac{2}{3}\sqrt{6}$ factor modifying the spin-spin constant λ deserves some comment. The parameter λ was first introduced by Hebb (17) in a consideration of spin-spin interactions in $^3\Sigma$ states, second order contributions to λ arising from the admixture of $^3\Pi$ states. The factor $\frac{2}{3}$ was included rather arbitrarily so as to simplify the arithmetical relation between λ and these second order terms, and as such is of no significance. It has now become traditional to write the magnitude of the spin-spin interaction as $\frac{2}{3}\lambda$, unnecessary though this may be. The $\sqrt{6}$ factor is by contrast a rigorous factor arising from the transformation from Cartesian to spherical tensor notation.

The linear molecule restriction (2.44) is readily appreciated by an examination of the vector coupling diagrams, as in diagram 1, but its mathematical justification is far from trivial (18). Because the third Euler angle is not present in linear molecules, the molecule-fixed components of the total angular momentum, J_x, J_y, J_z do not obey the usual commutation rules. Instead they commute with the anomalous sign of i :

$$\left[J_x, J_y\right] = -iJ_z \quad \text{etc.} \qquad (2.45)$$

Hougen (18) shows that a Hamiltonian including all three variables is isomorphic with the true rotational Hamiltonian provided a restriction on the additional variable is observed, this being the linear molecule restriction.

Second order contributions to the effective Hamiltonian arise from terms in V that mix different electronic states, namely the spin orbit coupling and L-uncoupling terms

$$-2BT^1(\underline{J}-\underline{S}).T^1(\underline{L}) + \sum_i T^1(a_i\,\underline{l}_i).T^1(\underline{s}_i)$$

$$= \qquad V_1 \qquad + \qquad V_2 \qquad (2.46)$$

$\underline{l}_i$ and $\underline{s}_i$ are the orbital and spin angular momenta of the i^{th} electron, the summation running over all the electrons of the molecule. The form of the spin-orbit term V_2 is simplified but is adequate for the present purposes. The true microscopic spin-orbit Hamiltonian (19, 20) describes the interaction of electron spins with the field due to electrons and nuclei, and so contains spin-orbit, spin-other-orbit and electronic screening effects. The selection rules arising from the simplified Hamiltonian are

$$\Delta\Omega = 0$$

$$\Delta S = 0, \pm 1$$

$$\Delta\Sigma = -\Delta\Lambda = \pm 1$$

but these in fact also apply to the true microscopic Hamiltonian. Using either form the correct parametric dependence of interactions is obtained but the interpretations of the constants differ.

Whereas in the spin-orbit interaction, all electrons have to be included in the summation, only unpaired electrons have to be considered in the spin-spin interaction. This is not an obvious point, and so will be considered in more detail.

McWeeny (21) has shown how the various parameters in the spin Hamiltonian can be written in terms of density functions (22) which describe the distribution of the electrons and the configuration of the spins. The operators in this spin Hamiltonian are written in terms of sums of 1- and 2-electron functions, since these are easier to visualise than the many-electron counterparts. The operators in the spin-spin dipolar interaction will thus be 2-electron operators, whereas the nuclear spin-electron spin interaction will only involve 1-electron operators. The spin-orbit interaction is rather more complicated since it involves the interaction of the electron spin with the magnetic field presented by all the electrons and nuclei, and as such involves both 1- and 2-electron operators. By use of Slater determinants it is possible to calculate matrix elements between individual spin-orbitals.

Consider first of all the matrix elements of a 1-electron operator, such as the nuclear spin-electron spin interaction. In its most general form this can be written

$$\sum_{i,\ k} e(i)n(k)$$

where e(i) is the spin density function for the i^{th} electron and n(k) a spin function for the k^{th} nucleus. If it is assumed that the 1-electron density functions for electrons of α and β spin represent similar distributions but are of opposite sign then it is easily seen that paired electrons give no net contribution to this interaction, so only the unpaired electrons need be considered.

The 2-electron interactions are more difficult to treat. Slater (23) has shown by expansion of Slater determinants how the matrix elements of a 2-electron operator reduce to a simple form. A Slater determinant takes the determinant form

$$\frac{1}{\sqrt{N!}}\begin{vmatrix} U_1(1) & U_2(1) \cdots\cdots & U_N(1) \\ U_1(2) & U_2(2) \cdots\cdots & U_N(2) \\ \vdots & \vdots & \\ U_1(N) & U_2(N) \cdots\cdots & U_N(N) \end{vmatrix} = \left| U_1\ U_2 \cdots\cdots U_N \right| \qquad (2.47)$$

where $U_i(N)$ represents the N^{th} electron occupying the i^{th} spin-orbital. As is well known, a determinant can be expanded in terms of the components of any row or column, the coefficient modifying each of these components being their corresponding cofactor, or signed minor. The minor M_{ij} of the element in the i^{th} row and j^{th} column is just the determinant remaining when the i^{th} row and j^{th} column are deleted from the full determinant.

The matrix elements of a 2-electron operator, g_{ij}, are then given by

$$\iint \left| U_1 \, U_2 \, . \, . \, . \, . \, U_N \right| g_{ij} \left| U_1' \, U_2' \, . \, . \, . \, . \, U_N' \right| d\tau_i \, d\tau_j \qquad (2.48)$$

which Slater has shown to reduce to the form

$$\sum_{i<j} M_{(ii')(jj')} \left\{ \langle U_i(1) U_j(2) | g_{12} | U_i'(1) U_j'(2) \rangle - \langle U_i(1) U_j(2) | g_{12} | U_j'(1) U_i'(2) \rangle \right\} \qquad (2.49)$$

The two matrix elements in (2.49) involve direct and exchange integrals respectively, $M_{(ii')(jj')}$ is the minor formed by deleting the i and i' rows and the j and j' columns. If we assume all the spin-orbitals are orthogonal to each other then all the minors in (2.49) are zero except for those corresponding to i = i' and j = j'.

In order to determine matrix elements of the spin-spin interaction an explicit form has to be substituted for g_{12}. We shall assume that this operator is of the general form

$$(\underline{s}_i \cdot \underline{s}_j - 3s_{iz} \, s_{jz}) \;\; \text{x} \;\; \text{orbital factor} \qquad (2.50)$$

and that matrix elements of this operator are in the same ratios as those of the spin only operator. This latter assumption is equivalent to the assumption that the matrix elements of (2.50) can be factored into a spin-dependent part and an orbital dependent part.

The spin-orbitals i, j correspond to either closed shell or open shell electrons and so there are four types of matrix element to be considered:

a) Both electrons in same closed shell;
b) Electrons in different closed shells;
c) One in a closed shell, one in an open shell;
d) Both electrons unpaired.

In case a) the direct and exchange integrals in (2.49) are equal in magnitude and opposite in sign so there is no contribution. Similarly in b), if i is a closed shell electron with a particular spin, say α, then the summation over j for the other causes this term to vanish. The term with i having β spin similarly vanishes. The contribution from c) also disappears, since if i is the open shell electron then the sum over j for the two allowed spin configurations of the other electron must be zero. The only remaining term, d), does not disappear since in general the direct and exchange terms are not of equal magnitude. Hence only unpaired electrons contribute to the spin-spin interaction.

The form of the spin-orbit interaction is much more complicated but from a general consideration of its physical significance it can be appreciated that all the electrons contribute. Only unpaired electrons contribute to the spin-spin interaction but in this case a specific form for the 2-electron operator has been used; the 2-electron operators present in the spin-orbit interaction do not necessarily reduce to this simple form and hence even the core electrons have to be included in the summations.

The second order Hamiltonian obtained from (2.46) is of the general form

$$H^{(2)}_{\text{eff}} = P_0V_1\,(Q_0/a)\,V_1P_0 + 2P_0V_1\,(Q_0/a)\,V_2P_0 + P_0V_2\,(Q_0/a)\,V_2P_0 \qquad (2.51)$$

By substituting the spherical tensor forms of (2.46) into (2.51) and factoring the resultant expression in terms of operator equivalents one can obtain the result

$$H^{(2)}_{\text{eff}} = B'T^1\,(\underline{J}-\underline{S}).\,T^1\,(\underline{J}-\underline{S}) + \gamma'T^1\,(\underline{J}-\underline{S}).\,T^1\,(\underline{S}) + \tfrac{2}{3}\sqrt{6}\,\lambda'T^2_0\,(\underline{S},\,\underline{S}) \qquad (2.52)$$

This expression has the same operator dependence as the first order Hamiltonian (2.43), the parameters B', γ' and λ' hence forming second order contributions to the rotational constant, spin-rotation constant and spin-spin constant respectively. The total effective Hamiltonian to second order is the sum of $H^{(1)}_{\text{eff}}$ and $H^{(2)}_{\text{eff}}$, the resultant being written in terms of the effective parameters:

$$\begin{aligned} B_{\text{eff}} &= B + B' \\ \gamma_{\text{eff}} &= \gamma + \gamma' \\ \lambda_{\text{eff}} &= \lambda + \lambda' \end{aligned} \qquad (2.53)$$

This is a familiar result (9, 24). Since each of the effective parameters is compounded from contributions from various orders of perturbation theory, care has to be taken in the interpretation of these constants, however.

In order to demonstrate some of the techniques discussed in the previous section, consider the calculation of the second order contribution to the spin-spin interaction in more detail. This term involves two matrix elements of the spin-orbit operator. From (2.46) and (2.51) we have:

$$H_{SS}^{(2)} = P_0 V_2 (Q_0/a) V_2 P_0$$

$$= P_0 \Big\{ \sum_{\eta'\Lambda'} \sum_{S'\Sigma'} \left(E^0_{\eta\Lambda} - E^0_{\eta'\Lambda'} \right)^{-1}$$

$$\times \Big[\sum_q (-1)^q (-1)^{S-\Sigma} \begin{pmatrix} S & 1 & S' \\ -\Sigma & q & \Sigma' \end{pmatrix} \sum_i \langle \eta \Lambda S \| T^1(\underline{s}_i)\, T^1_{-q}(a_i \underline{l}_i) \| \eta'\Lambda' S' \rangle \Big]$$

$$\times \Big[\sum_{q'} (-1)^{q'} (-1)^{S'-\Sigma'} \begin{pmatrix} S' & 1 & S \\ -\Sigma' & q' & \Sigma'' \end{pmatrix} \sum_j \langle \eta'\Lambda' S' \| T^1(\underline{s}_j) T^1_{-q'}(a_j \underline{l}_j) \| \eta \Lambda'' \rangle \Big] \Big\} P_0 \qquad (2.54)$$

This can be simplified for a Σ state by putting $\Lambda'' = \Lambda$ (= 0) and $\Sigma'' = \Sigma$. The latter simplification follows from the $\Delta\Omega = 0$ selection rule governing the spin-orbit interaction. Since the effective Hamiltonian operates only within a particular vector space then this operator should make no reference to other electronic states. The excited state quantum numbers S' and Σ' that appear in equation (2.54) have therefore to be suppressed, and so with this end in mind, the pair of 3-j symbols in (2.54) are reexpressed by making use of equation (2.39). The following relation is obtained:

$$\begin{pmatrix} S & 1 & S' \\ -\Sigma & q & \Sigma' \end{pmatrix} \begin{pmatrix} S' & 1 & S \\ -\Sigma' & q & \Sigma \end{pmatrix} = (-1)^{S-\Sigma} \sum_k (2k+1) \begin{pmatrix} S & S & k \\ -\Sigma & \Sigma & 0 \end{pmatrix} \begin{pmatrix} 1 & 1 & k \\ q & -q & 0 \end{pmatrix} \begin{Bmatrix} S & S & k \\ 1 & 1 & S' \end{Bmatrix} \qquad (2.55)$$

The relation q' = −q arises from the sum rules of the 3-j symbols.

Equation (2.54) thus becomes

$$H_{SS}^{(2)} = P_0 \Big\{ \sum_{\eta'\Lambda'} \sum_{S'\Sigma'} (E^0_{\eta\Lambda} - E^0_{\eta'\Lambda'})^{-1} (-1)^{S-\Sigma} \sum_k (2k+1) \begin{pmatrix} S & S & k \\ -\Sigma & \Sigma & 0 \end{pmatrix} \begin{Bmatrix} S & S & k \\ 1 & 1 & S' \end{Bmatrix}$$

$$\sum_{i,\ j} \sum_{q} \begin{pmatrix} 1 & 1 & k \\ q & -q & 0 \end{pmatrix} \langle \eta\Lambda S \| T^{1}(\underline{s}_i) T^{1}_{-q}(a_i \underline{l}_i) \| \eta'\Lambda' S' \rangle \langle \eta'\Lambda' S' \| T^{1}(\underline{s}_j) T^{1}_{q}(a_j \underline{l}_j) \| \eta\Lambda S \rangle \Big\} P_0 \tag{2.56}$$

From the triangle rules on the 3-j and 6-j symbols it is now possible to make some useful restrictions. The rank k can take only the values

$$k = 0,\ 1 \text{ or } 2$$

Substituting $k = 0$ into (2.56) shows that this term has no Σ dependence and so does not affect the relative energies of the rotational levels. This term is of the form of the spin-spin interaction, which is generally absorbed into the electronic energy.

If q is replaced by -q in the 3-j symbol $\begin{pmatrix} 1 & 1 & k \\ q & -q & 0 \end{pmatrix}$ the symmetry properties of 3-j symbols show that its value is multiplied by $(-1)^k$. Since for a Σ state the pair of reduced matrix elements do not change sign on replacing q by -q then the effect on the total expression is to multiply it by $(-1)^k$. The summation over q values thus causes the $k = 1$ term to vanish.

The only remaining term is that with $k = 2$, which can be written

$$H^{(2)}_{k=2} = (-1)^{S-\Sigma} \begin{pmatrix} S & 2 & S \\ -\Sigma & 0 & \Sigma \end{pmatrix} P_0 \Big[\sum_{\eta'\Lambda'} \sum_{S'\Sigma'} (E^0_{\eta\Lambda} - E^0_{\eta'\Lambda'})^{-1}\, 5 \begin{Bmatrix} S & S & 2 \\ 1 & 1 & S' \end{Bmatrix}$$

$$\times \sum_{i,\ j} \sum_{q} \begin{pmatrix} 1 & 1 & 2 \\ q & -q & 0 \end{pmatrix} \langle \eta\Lambda S \| T^{1}(\underline{s}_i) T^{1}_{-q}(a_i \underline{l}_i) \| \eta'\Lambda' S' \rangle$$

$$\langle \eta'\Lambda' S' \| T^{1}(\underline{s}_j) T^{1}_{q}(a_j \underline{l}_j) \| \eta\Lambda S \rangle \Big] P_0 \tag{2.57}$$

This term is of the form of the dipolar spin-spin interaction, which as has already been noted, is a second rank tensor interaction. Matrix elements of this interaction are of the form

$$\langle S\Sigma | \tfrac{2}{3}\sqrt{6}\,\lambda T^{2}_{0}(\underline{S},\ \underline{S}) | S\Sigma \rangle = (-1)^{S-\Sigma} \begin{pmatrix} S & 2 & S \\ -\Sigma & 0 & \Sigma \end{pmatrix} \tfrac{2}{3}\sqrt{6}\,\lambda \langle S \| T^{2}(\underline{S},\ \underline{S}) \| S \rangle \tag{2.58}$$

Comparison of (2.57) and (2.58) shows that these expressions both involve a similar dependence on quantum numbers, and so the term in square braces in (2.57) can be equated with $\frac{2}{3}\sqrt{6}\,\lambda' \langle S \| T^{2}(\underline{S},\ \underline{S}) \| S \rangle$, where λ' is the second order contribution to the spin-spin interaction constant.

Further information can yet be gleaned from the 3-j and 6-j symbols. The triangle rules on $\begin{pmatrix} S & 2 & S \\ -\Sigma & 0 & \Sigma \end{pmatrix}$ restrict the values of S to $S \geqslant 1$, which is well known, since spin-spin interactions can arise only when there are two or more unpaired electrons. Similarly from the 6-j symbol in (2.57), the allowed values of S' are obtained, namely S' = S + 1, S, S - 1 only, a result which follows also from the selection rules on the spin-orbit coupling interaction.

This completes the derivation of the second order spin-spin Hamiltonian, the calculation of the other terms in the second order Hamiltonian following along similar lines.

It must be emphasised that no part of this chapter is new; its contents serve merely as useful groundwork for later chapters.

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CHAPTER 3

SPIN-DEPENDENT INTERACTIONS IN Σ STATES OF QUARTET AND HIGHER MULTIPLICITY

3.1 Introduction

As has been discussed in chapter 2, in the analysis of molecular spectra we wish to calculate the energy levels as accurately as necessary but at the same time it is necessary to restrict the problem to one of manageable size. In the case of transitions occuring within a single electronic state, such as in microwave or e.p.r. spectroscopy, this requirement can be met by constructing an effective Hamiltonian that operates only within that particular state. Transitions occurring between electronic states, such as in optical spectroscopy, can be dealt with in a similar manner by constructing two effective Hamiltonians, one for each of the states involved. The difficulty lies in deriving a suitable effective Hamiltonian, that is to say, one that leads to an adequate description of the energy levels.

The technique of constructing effective Hamiltonians used here is, as already described, to use degenerate perturbation theory to incorporate terms off-diagonal in electronic state into the diagonal blocks and subsequently to rewrite the perturbation expressions in terms of operator equivalents. This has been demonstrated in the previous chapter, the calculation of the second order contribution to the spin-spin interaction being given as an example.

In this chapter the form and number of effective parameters needed to describe Σ electronic states of various multiplicities for linear molecules is investigated, in particular for those Σ states of quartet and higher multiplicity (1). The possible presence of nuclear spins will be ignored throughout this treatment, as will the effects of centrifugal distortion.

The rotational levels of a linear molecule in a $^1\Sigma$ state are given by the familiar term value expression

$$F = B\,J\,(J + 1) \qquad (3.1)$$

where B is the rotational constant and J is the total angular momentum quantum number. The term value expressions become more complicated for molecules in states of higher multiplicity than singlet since further parameters are required to describe the additional interactions arising from the unpaired electron spins.

In a $^2\Sigma$ state the effects of the spin-rotation interaction have to be included, the parameter needed to describe this interaction being γ, whereas in a $^3\Sigma$ state the effects of a spin-spin interaction, described by the parameter λ, have also to be considered.

The parameters B, γ and λ describe interations that occur only within the particular electronic state under consideration, and consequently will be compounded of both direct and indirect contributions, the latter arising from the perturbation treatment of nonadiabatic terms in the total Hamiltonian, such as Coriolis and spin-orbit interactions, (2).

The dependence of the rotational energy levels on these parameters is in accordance with that observed in molecular spectra, which justifies the form of the effective Hamiltonian that has been used in the analyses of these states. In addition, the interpretation of these constants in terms of electronic structure is fairly well understood, although it should be noted that the higher order perturbation contributions complicates the interpretation considerably.

In the case of $^4\Sigma$ states, the understanding of the effective parameters is less certain. The first investigation of $^4\Sigma$ states was performed by Budó (3), who was able to arrive at term value expressions for the rotational energy levels. Similar results were subsequently obtained by Budó and Kovács (4) using a different approach. Budó's expressions have been quite widely used, giving adequate analyses of data in some cases. However, Verma (5), in an analysis of the SiF radical found that these expressions were not satisfactory. This prompted Hougen (6) to reinvestigate the energy level expressions. He used an approach similar to that of Budó and Kovács (4), involving an examination of the effects of spin-orbit coupling, and was able to obtain more general expressions for the rotational energy levels. He reached the general conclusion that in Σ states of even multiplicity, $(2S + 1)$, $(S + \frac{1}{2})$ spin-rotation parameters and $(S - \frac{1}{2})$ spin-spin parameters are required, while for a state of odd multiplicity S spin-rotation and S spin-spin parameters have to be included. To describe the energy levels of a $^4\Sigma$ state one spin-spin parameter (λ) and two spin-rotation parameters would thus be needed. Since the molecules of interest contain heavy atoms then spin-orbit coupling will be large and so a convenient choice of basis functions would be one conforming to Hund's case a) coupling. The basis kets are thus of the form

$$| \eta \Lambda ; S \Sigma ; J \Omega M >$$

Consider the effects of the perturbation Hamiltonian on the molecular energy levels: in the absence of rotation, the spin-spin and spin-orbit interactions cause a splitting of the $^4\Sigma$ level into two double degenerate components, labelled $^4\Sigma_{3/2}$ and $^4\Sigma_{1/2}$, where the subscript represents the value of $|\Omega|$, the spin splitting for $^4\Sigma$ states being 4λ. If rotation is included then the effects of the spin-rotation interaction lift the degeneracy of these components leading to four fine-structure states, $^4\Sigma_{3/2}$, $^4\Sigma_{1/2}$, $^4\Sigma_{-1/2}$ and $^4\Sigma_{-3/2}$ the subscript in this case being Ω. Each of these four states possesses an infinite set of rotational levels, labelled J, subject to the restriction $J \geqslant |\Omega|$. The energy levels are illustrated in figure 1 for the case of a regular $^4\Sigma$ state, i.e. $(\lambda - 2B) > 0$, so for a given J $^4\Sigma_{1/2}$ levels lie below $^4\Sigma_{3/2}$ levels. For inverted states the reverse applies.

Hougen (6) defines the two spin-rotation constants as γ_1 and γ_2 where γ_1 appears in the matrix element

$$\langle J; \Omega = \pm 1/2 \,|H_{SR}|\, J; \Omega = \mp 1/2 \rangle \qquad (3.2)$$

and γ_2 appears in the element

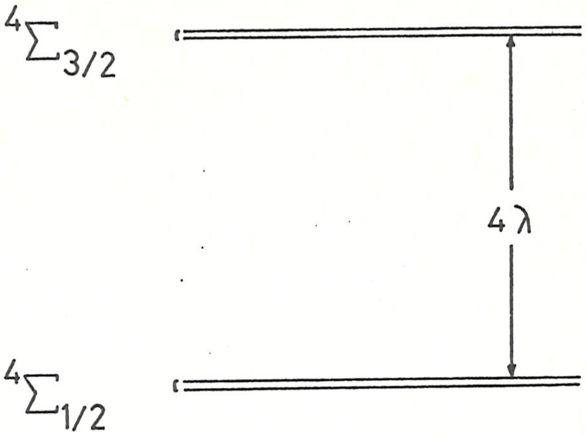
$$\langle J; \Omega = \pm 3/2 \,|H_{SR}|\, J; \Omega = \pm 1/2 \rangle \qquad (3.3)$$

where H_{SR} is the spin-rotation Hamiltonian.

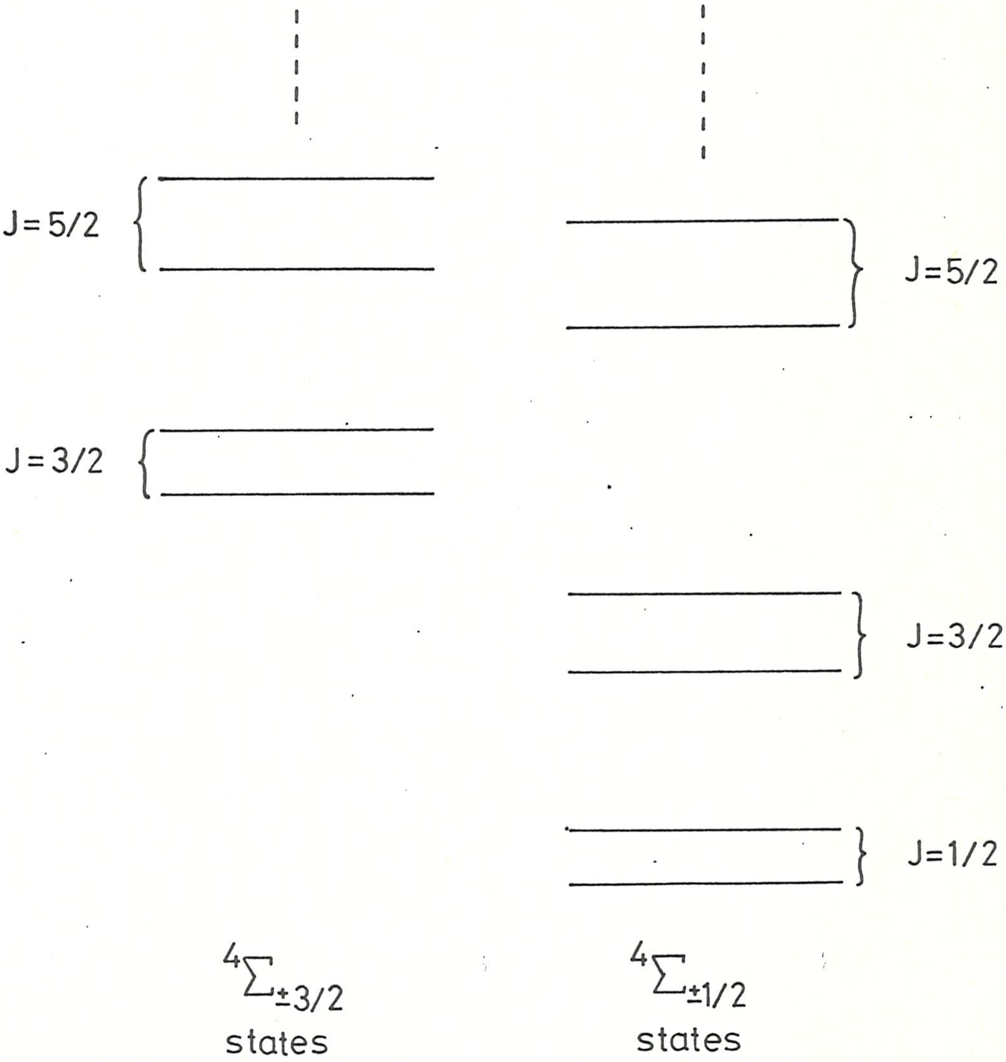
Very few detailed analyses of molecules in $^4\Sigma$ states have been published; all the data obtained so far come from optical spectra of diatomic molecules, the molecules being O_2^+ (7), SiF (5, 8), GeF (9), SnH (10), GeH (11) and VO (12). In those cases that have been treated using Hougen's expressions, the values obtained for γ_1 and γ_2 are the same to within experimental error, even for SiF. The discrepancies in this spectrum that prompted Hougen to reinvestigate the $^4\Sigma$ rotational levels have been shown by Martin and Merer (8) to arise from misassignments of the original data.

Hougen's γ parameters are introduced by general consideration of the various types of matrix elements that contain contributions from the spin-rotation interaction and in this respect are purely intuitive. It is expected that the difference between γ_1 and γ_2 is related to higher order terms in the perturbation expansion, thus reflecting different mixings with other electronic states. In the following sections the form of these parameters is investigated by a consideration of such higher order terms, so that the difference between them can be related to more fundamental molecular parameters.

Figure 1 Schematic representation of energy levels in a $^4\Sigma$ state.



a) Absence of rotation



b) Rotation included

In the final section of this chapter the treatment of effective parameters is extended to $^5\Sigma$ states, paying particular attention to an additional spin-spin interaction that arises in fourth order of perturbation theory.

3.2 General Form of Third-Order Spin-Rotation Interactions in $^4\Sigma$ states

The spin-rotation interaction to second order is of the form

$$H_{SR} = \gamma_{eff}\, T^1\,(\underline{J} - \underline{S}) \cdot T^1\,(\underline{S}) \qquad (3.4)$$

where $\gamma_{eff} = \gamma^{(1)} + \gamma^{(2)}$, the sum of first and second order contributions. The two types of matrix element of this Hamiltonian, equations (3.2) and (3.3), involve only this single γ parameter, so to determine the difference between γ_1 and γ_2 higher order terms must be investigated. In this section the third order contributions will be calculated.

The general form of the third order Hamiltonian can be found from equation (2.24) of chapter 2 and in its Hermitian averaged form is as follows:

$$\begin{aligned} H_{eff}^{(3)} &= P_0 V U^{(3)} \\ &= P_0 V\, (Q_0/a)\, V\, (Q_0/a)\, V P_0 \\ &- \tfrac{1}{2}\left\{ P_0 V\, (Q_0/a^2)\, V P_0 V P_0 + P_0 V P_0 V\, (Q_0/a^2)\, V P_0 \right\} \qquad (3.5) \end{aligned}$$

Only those terms in the perturbation Hamiltonian that ultimately give rise to an effective spin-rotation interaction are of interest. By inspection of the terms in this Hamiltonian

$$V = H_{ROT} + H_{SS} + H_{SR} + H_{SO}$$

it can be seen that third-order spin-rotation terms arise in three different ways, as illustrated in figure 2 by means of some typical 'railroad' diagrams. They are comprised of three matrix elements of V in the following manner:

a) (spin-orbit interaction)^2 (spin-uncoupling)
b) (spin-orbit interaction) (L-uncoupling) (rotational interaction)
c) (L-uncoupling)^2 (spin-uncoupling)

The L-uncoupling terms come from H_{ROT} and are of the form

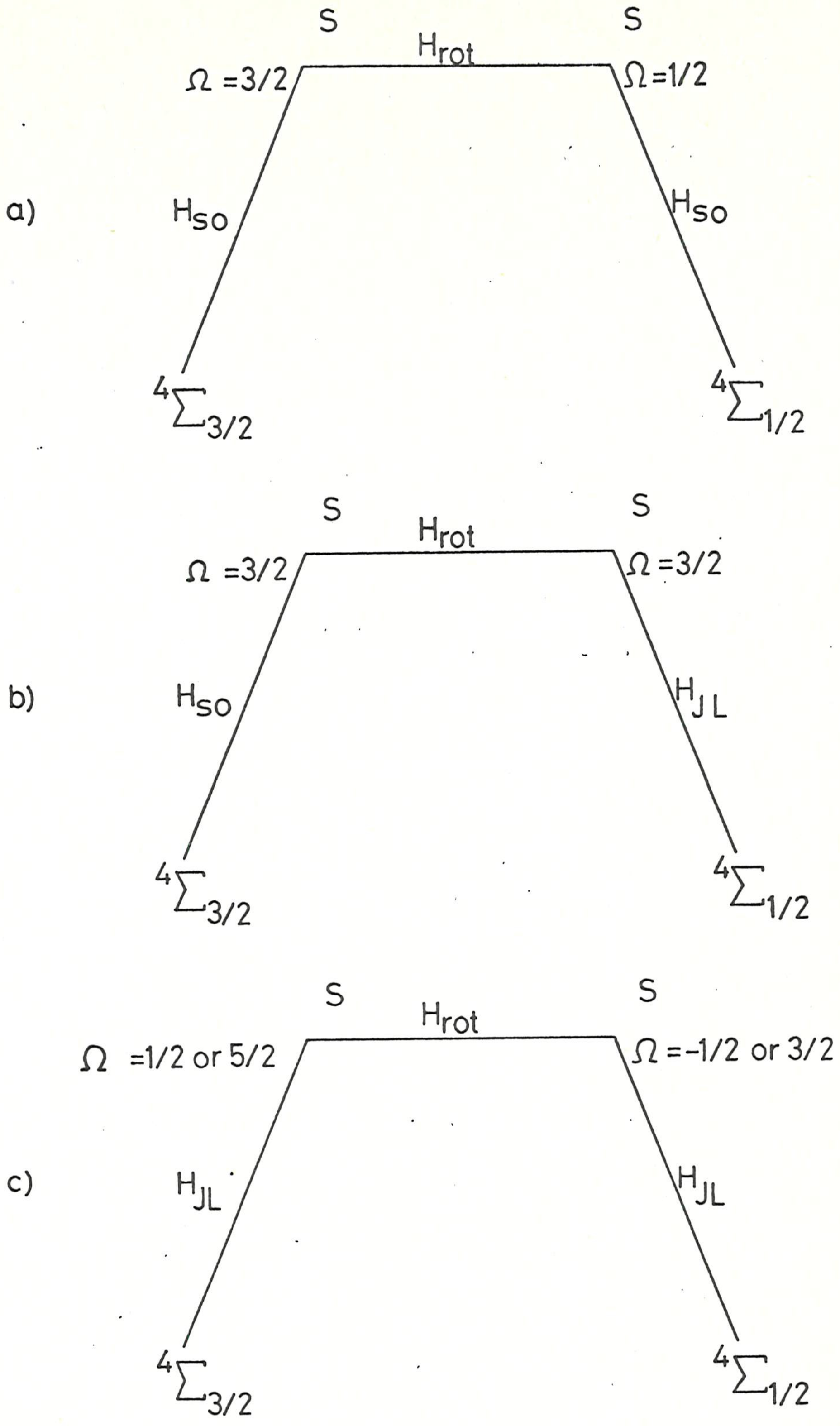


Figure 2 Some third order contributions to the spin-rotation interaction in a $^4\Sigma$ state.

$$-2B \sum_{q=\pm 1} T^1_q(\underline{J})\, T^1_{-q}(S) \qquad (3.7)$$

while "rotational interaction" refers to the q = 0 terms from H_{ROT}

$$B\left[J(J + 1) + S(S + 1) - \Omega^2 - \Sigma^2 \right] \qquad (3.8)$$

Note that although all three of the terms above are spin-rotation interactions, they each have a different J dependence, their respective operator forms being $J_\alpha S^3_\beta$, $J^2_\alpha S^2_\beta$ and $J^3_\alpha S_\beta$. If A is taken to be the spin-orbit coupling constant and ΔE is some measure of the difference in energy origins of the ground and admixed states, then the approximate magnitudes of the three contributions above are

a) $A^2B/(\Delta E)^2$
b) $AB^2/(\Delta E)^2$
c) $B^3/(\Delta E)^2$

Since the spin-orbit coupling constant for these $^4\Sigma$ molecules is much larger than the rotational constant then the dominant contribution will be from a), that involving two matrix elements of H_{SO} between electronic states and one matrix element of the spin uncoupling interaction. The matrix elements of the spin-uncoupling operator are of exactly the same form as those of the spin-rotation Hamiltonian and so there will be third order contributions to a) and c) of magnitudes $A^2\gamma/(\Delta E)^2$ and $B^2\gamma/(\Delta E)^2$ respectively. These however will be inseparable from the corresponding contributions involving the spin-uncoupling operator. In principle, since the three types of contribution in third order have different J and S dependencies, then these different third order terms are separable. However, only the dominant contribution a) will be considered as it is likely that any difference in γ_1 and γ_2 will arise predominantly from this term.

Application of the selection rules for spin-orbit coupling, given in chapter 2, reveals that the only states that could be mixed into a $^4\Sigma$ state in third order by mechanism a) are the following: $^2\Sigma$, $^2\Pi$, $^4\Pi$, $^6\Sigma$, $^6\Pi$ or another $^4\Sigma$ state. Some examples of the contamination of $^4\Sigma$ states in third order by states mixed in this manner are shown in figure 3.

Substitution of the matrix elements of the relevant perturbation terms into equation (3.5) leads to the following expression:

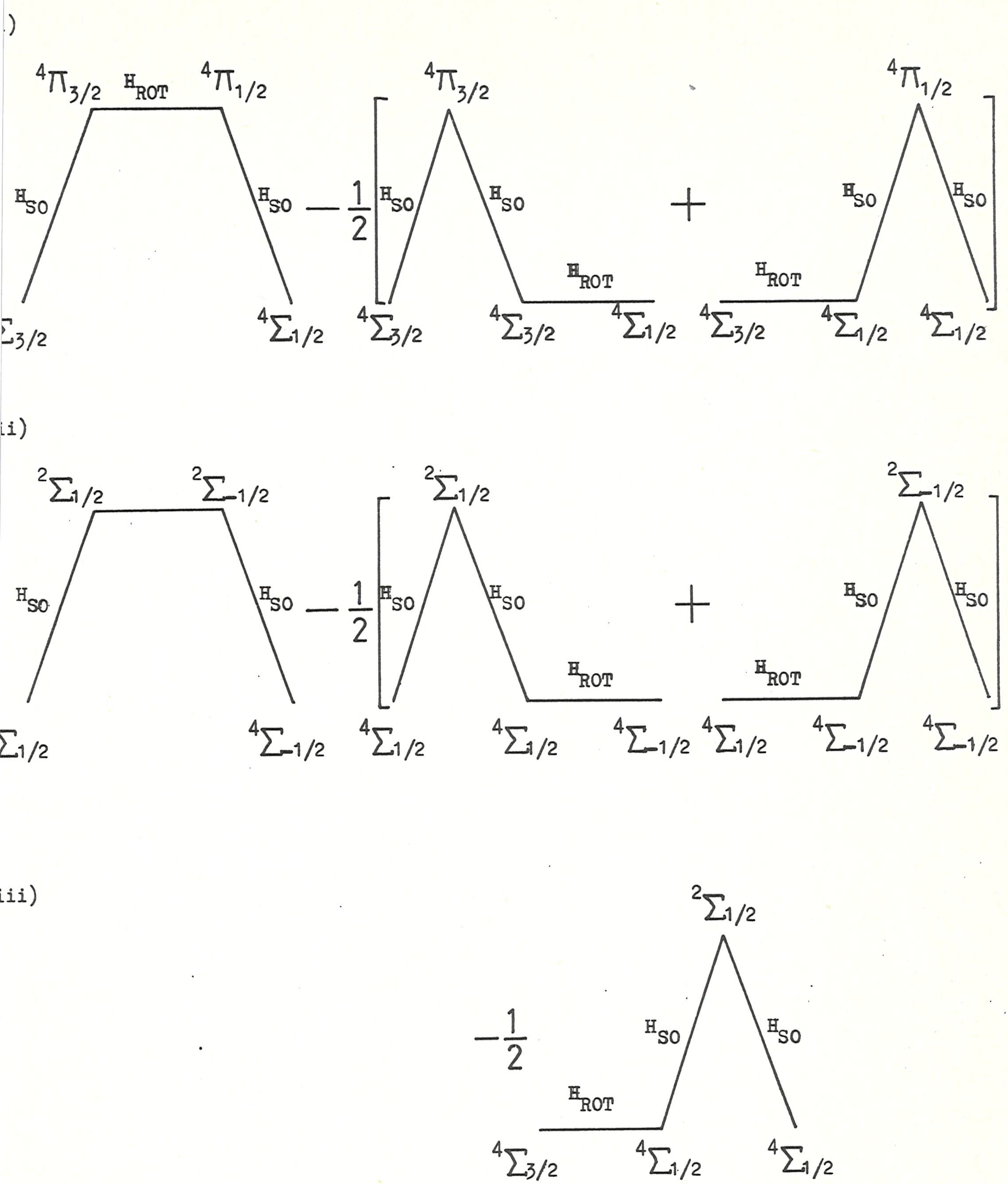


Figure 3 Some third order interactions giving rise to effective spin-rotation interactions.

i) Admixture of $^4\Pi$ states.
ii) and iii) Admixture of $^2\Sigma$ states.

$$\begin{aligned}
&\langle \eta \Lambda ;\ S\Sigma ;\ J\Omega M |\, H_{SR}^{(3)} \,| \eta \Lambda ;\ S\Sigma'' ;\ J\Omega'' M \rangle = \\
&\sum_{q,\ q'} (-1)^{J-\Omega} \begin{pmatrix} J & 1 & J \\ -\Omega & q' & \Omega'' \end{pmatrix} \left[J(J+1)(2J+1) \right]^{\frac{1}{2}} (E^{0}_{\eta\Lambda S} - E^{0}_{\eta'\Lambda' S'})^{-2} \\
&|\langle \eta \Lambda S \| \sum_{i} T^{1} (\underline{s}_i)\, T^{1}_{q} (a_i \underline{l}_i) \| \eta' \Lambda' S' \rangle|^{2} \Bigg\{ \Bigg[-2B' \left[S'(S'+1)(2S'+1) \right]^{\frac{1}{2}} \\
&(-1)^{S-\Sigma} \begin{pmatrix} S & 1 & S' \\ -\Sigma & -q & \Sigma' \end{pmatrix} (-1)^{S'-\Sigma'} \begin{pmatrix} S' & 1 & S' \\ -\Sigma' & q' & \Sigma''' \end{pmatrix} (-1)^{S'-\Sigma'''} \begin{pmatrix} S' & 1 & S \\ -\Sigma''' & q & \Sigma'' \end{pmatrix} \Bigg] \\
&-\tfrac{1}{2} \Bigg(-2B \left[S(S+1)(2S+1) \right]^{\frac{1}{2}} \Bigg\{ \Bigg[(-1)^{S-\Sigma} \begin{pmatrix} S & 1 & S' \\ -\Sigma & -q & \Sigma' \end{pmatrix} (-1)^{S'-\Sigma'} \begin{pmatrix} S' & 1 & S \\ -\Sigma' & q & \Sigma \end{pmatrix} \\
&(-1)^{S-\Sigma} \begin{pmatrix} S & 1 & S \\ -\Sigma & q' & \Sigma'' \end{pmatrix} \Bigg] + \Bigg[(-1)^{S-\Sigma} \begin{pmatrix} S & 1 & S \\ -\Sigma & q' & \Sigma'' \end{pmatrix} (-1)^{S-\Sigma''} \begin{pmatrix} S & 1 & S' \\ -\Sigma'' & -q & \Sigma'' \end{pmatrix} \\
&(-1)^{S-\Sigma''} \begin{pmatrix} S' & 1 & S \\ -\Sigma'' & q & \Sigma \end{pmatrix} \Bigg] \Bigg\} \Bigg) \Bigg\}
\end{aligned} \tag{3.9}$$

where $q(= 0, \pm 1)$ is the component of the spin-orbit coupling operator,

$q'(= \pm 1$ only) is the component of the spin-uncoupling operator,

B and B' are the rotational constants in the $^4\Sigma$ and admixed electronic states respectively.

The various primed and unprimed quantum numbers in (a) apply to different electronic states and have the significance shown in figure 4. Equation (3.8) can be rewritten by invoking equation (2.39) of chapter 2 twice, so as to contract the 3-j symbols and to remove the dependence on intermediate spin quantum numbers, leading to the following expression:

$$\begin{aligned}
&\langle \eta \Lambda S \Sigma J \Omega M |\, H_{SR}^{(3)} | \eta \Lambda S \Sigma'' J \Omega'' M \rangle = \\
&-2 \sum_{q' = \pm 1} (-1)^{J-\Omega} \begin{pmatrix} J & 1 & J \\ -\Omega & q' & \Omega'' \end{pmatrix} \left[J(J+1)(2J+1) \right]^{\frac{1}{2}} \sum_{k,\ k} (-1)^{S-\Sigma} \\
&x \begin{pmatrix} S & K & S \\ -\Sigma & q' & \Sigma'' \end{pmatrix} (2k+1)(2K+1) \sum_{\substack{\eta'\Lambda' S' \\ (q)}} (E^{0}_{\eta\Lambda S} - E^{0}_{\eta'\Lambda' S'})^{-2} (-1)^{q} \\
&(-1)^{S-\Sigma+S'-\Sigma} |\langle \eta \Lambda S \| \sum_{i} T^{1} (\underline{s}_i)\, T^{1}_{q} (a_i \underline{l}_i) \| \eta' \Lambda' S' \rangle|^{2}
\end{aligned}$$

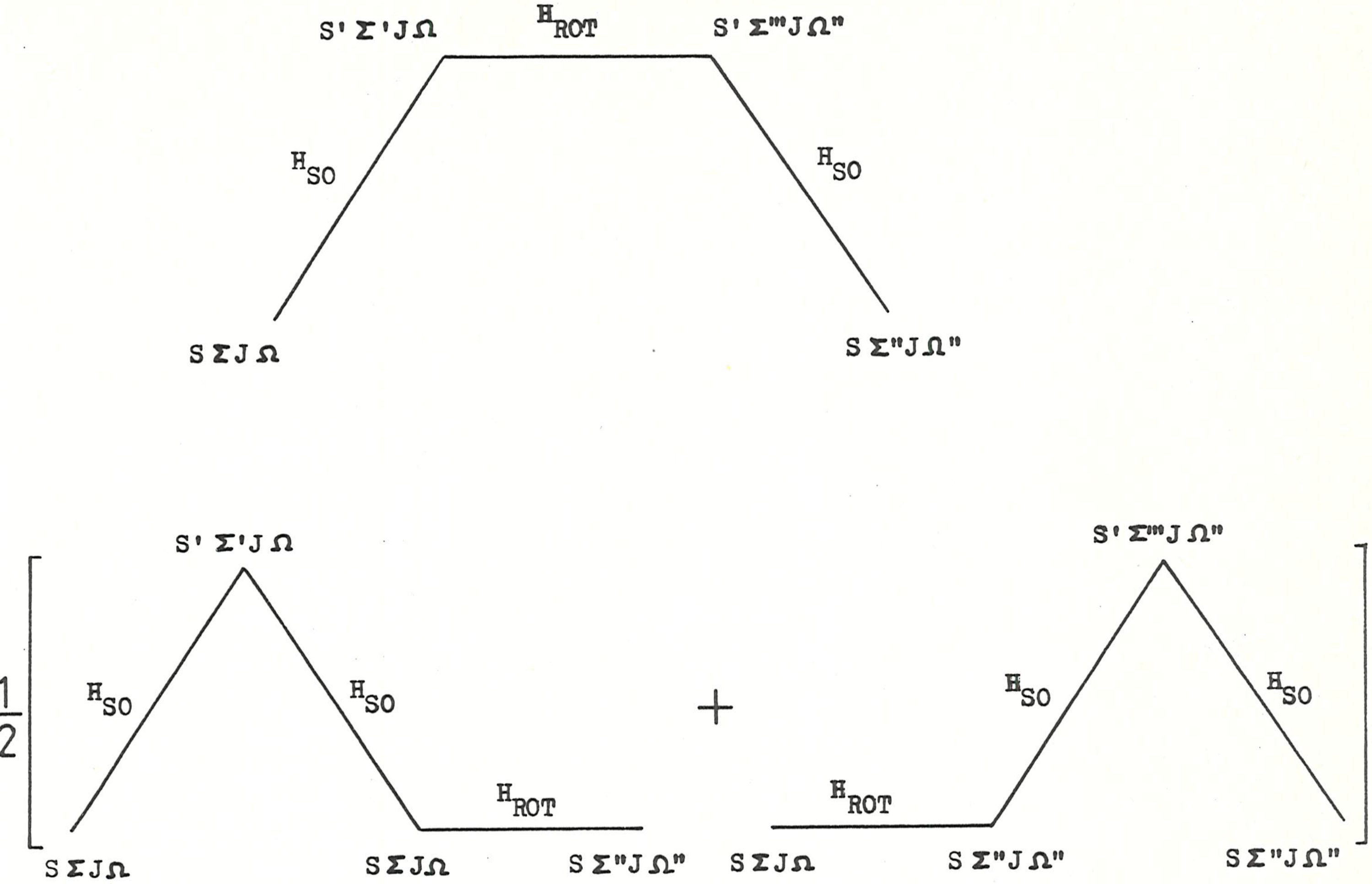


Figure 4 Notation used for calculation of third order terms.

$$\times \begin{Bmatrix} 1 & k & K \\ S & S & S' \end{Bmatrix} \begin{pmatrix} 1 & k & K \\ q & -q-q' & q' \end{pmatrix} \begin{pmatrix} 1 & 1 & k \\ -q & -q' & q+q' \end{pmatrix} \Big\{ (-1)^{1+k+K} \quad B'\left[S'(S'+1)(2S'+1)\right]^{\frac{1}{2}}$$

$$\times \begin{Bmatrix} S & S' & S' \\ 1 & 1 & k \end{Bmatrix} -\tfrac{1}{2}\left[1 + (-1)^{K+1}\right] \begin{Bmatrix} S & S' & S \\ 1 & 1 & k \end{Bmatrix} B\left[S(S+1)(2S+1)\right]^{\frac{1}{2}} \Big\} \qquad (3.10)$$

The tensor ranks k and K result from the first and second contractions of 3-j symbols respectively. The values k and K are permitted to take are governed by the triangle rules on the 3-j (or 6-j) symbols and are given in table 1.

3.3 Simplification of the General Third Order Spin-Rotation Terms

In this section we consider the various terms that arise from (3.10) on substitution of the allowed values of the tensor ranks k and K.

Since we are considering $q' = \pm 1$ only then the 3-j symbol $\begin{pmatrix} 1 & k & K \\ q & -q-q' & q' \end{pmatrix}$ is zero for K = 0. Hence K = 0 terms will not be considered further.

In order to cast equation (3.10) into operator equivalent form, values of k and K have to be substituted explicitly and individual terms examined. Consider, first of all, those terms with K even. The factor $1 + (-1)^{K+1}$ modifying the second term within the braces in (3.10) is seen to be zero for K even and so only the first term within braces remains. By relating the term with +q to that with −q it is possible to show that this term also disappears. With this end in mind, consider the k- and q- dependent factors in (3.10)

$$\sum_{k} (2k+1)(-1)^{q} \left| \langle \eta \Lambda S \| \sum_{i} T^{1}(\underline{s}_i)\, T^{1}_{q}(a_i \underline{l}_i) \| \eta' \Lambda' S' \rangle \right|^{2}$$

$$\times \begin{Bmatrix} 1 & 1 & k \\ S & S' & S' \end{Bmatrix} \begin{Bmatrix} 1 & k & K \\ S & S & S' \end{Bmatrix} \begin{pmatrix} 1 & 1 & k \\ q' & q & -q-q' \end{pmatrix} \begin{pmatrix} 1 & k & K \\ -q & q+q' & -q' \end{pmatrix} \qquad (3.11)$$

which we wish to show to vanish when summed over k and q. The reduced matrix elements in (3.11) are the same for both +q and −q, but <u>only</u> for Σ states, since then we have

$$\left| \langle \Sigma \mid q = +1 \mid \Pi, \Lambda = 1 \rangle \right|^{2} = \left| \langle \Sigma \mid q = -1 \mid \Pi, \Lambda = -1 \rangle \right|^{2}$$

The two 6-j symbols can be reexpressed by using the Biedenharn-Elliot relationship, a general relation given in equation (2.40) of chapter 2, to give the following:

k	K
0	1
1	0,1,2
2	1,2,3

Table 1 Allowed values for the tensor ranks k and K in the calculation of third-order contributions to the spin-rotation interaction.

$$\begin{Bmatrix} S & S' & 1 \\ 1 & k & S' \end{Bmatrix} \begin{Bmatrix} 1 & S & K \\ S & k & S' \end{Bmatrix} = \sum_{j} (-1)^{K+k+j+1} \quad (2j + 1)$$

$$\times \begin{Bmatrix} 1 & S' & S' \\ S & 1 & j \end{Bmatrix} \begin{Bmatrix} S' & S & 1 \\ K & j & S \end{Bmatrix} \begin{Bmatrix} 1 & 1 & k \\ K & 1 & j \end{Bmatrix} \qquad (3.12)$$

j is defined by the triangle rules on the 6-j symbols and is easily seen from the final symbol to take the same set of values as k, namely

$$j = 0, 1 \text{ or } 2 \text{ only.}$$

Whereas K represents the tensor rank of the final coupling of electron spins, both k and j represent some intermediate coupling of spins; k and j might differ in the order in which the spins are coupled.

All that remains is to relate the 3-j symbols with +q to those with -q. These can be contracted using equation (2.39) of chapter 2 and rearranged to give

$$\begin{pmatrix} 1 & 1 & k \\ q' & q & -q-q' \end{pmatrix} \begin{pmatrix} 1 & k & K \\ -q & q+q' & -q' \end{pmatrix} = \sum_{j} (2j + 1) \begin{Bmatrix} 1 & 1 & j \\ K & 1 & k \end{Bmatrix} (-1)^{k+j}$$

$$\times \begin{pmatrix} 1 & 1 & j \\ q' & -q & q-q' \end{pmatrix} \begin{pmatrix} 1 & j & K \\ q & -q+q' & -q' \end{pmatrix} \qquad (3.13)$$

where again j is defined by the triangle rules. The pair of 3-j symbols on the right-hand side differs from those on the left-hand side in that they contain the rank j instead of k, and q is replaced by -q throughout. By substituting (3.13) into (3.11) and using the Biedenharn-Elliot relationship (3.12) in reverse, an expression relating the term with +q and intermediate rank k to that with -q and intermediate rank j is obtained. Since k and j take the same values (0, 1 and 2 only) and since each side of the aforementioned expression contains a summation over either k or j, then it is justifiable to set j = k throughout. An expression is therefore obtained which relates the matrix element with +q to that with -q:

$$\sum_{k} (2k + 1)(-1)^{q} \left| \langle \eta \Lambda S \| \sum_{i} T^{1} (\underline{s}_{i})\, T^{1}_{q} (a_{i}\underline{l}_{i}) \| \eta' \Lambda' S' \rangle \right|^{2} \begin{Bmatrix} 1 & 1 & k \\ S & S' & S' \end{Bmatrix}$$

$$\times \begin{Bmatrix} 1 & k & K \\ S & S & S' \end{Bmatrix} \begin{pmatrix} 1 & 1 & k \\ q' & q & -q-q' \end{pmatrix} \begin{pmatrix} 1 & k & K \\ -q & q+q' & -q' \end{pmatrix}$$

$$= (-1)^{K+1} \sum_{k} (2k + 1)(-1)^{q} \left| \langle \eta \Lambda S \| \sum_{i} T^{1} (\underline{s}_{i})\, T^{1}_{-q} (a_{i}\underline{l}_{i}) \| \eta' \Lambda' S' \rangle \right|^{2}$$

$$\times \begin{Bmatrix} 1 & 1 & k \\ S & S' & S' \end{Bmatrix} \begin{Bmatrix} 1 & k & K \\ S & S & S' \end{Bmatrix} \begin{pmatrix} 1 & 1 & k \\ q' & -q & q-q' \end{pmatrix} \begin{pmatrix} 1 & k & K \\ q & q'-q & -q' \end{pmatrix} \qquad (3.14)$$

Substitution of q = 0 into (3.14) reveals that contributions with K even vanish. Similarly, the terms with K even disappear on substituting $q = \pm 1$ and summing over q. We thus have the general result that all even K contributions to the spin-rotation interaction vanish in third order.

Consider now the contributions from (3.9) with K odd. It can easily be shown that

$$\left[S'(S'+1)(2S'+1)\right]^{\frac{1}{2}}\begin{Bmatrix}1 & 1 & k\\ S & S' & S'\end{Bmatrix} = \left[S(S+1)(2S+1)\right]^{\frac{1}{2}}\begin{Bmatrix}1 & 1 & k\\ S' & S & S\end{Bmatrix} \tag{3.15}$$

for k = 0 and 2 (but not for k = 1): expansion of the 6-j symbols shows that for k = 0 and 2, interchange of the symbols S and S' does not affect the value of the expression, whereas for k = 1 this interchange alters the arithmetical value.

The term within braces in equation (3.10) thus becomes, for k even and K odd,

$$\left\{(-1)^{1+k+K}B' - \tfrac{1}{2}\left[1+(-1)^{K+1}\right]B\right\}\left[S(S+1)(2S+1)\right]^{\frac{1}{2}}\begin{Bmatrix}1 & 1 & k\\ S & S' & S\end{Bmatrix}$$

$$= \triangle B \;\; S(S+1)(2S+1)^{\frac{1}{2}}\begin{Bmatrix}1 & 1 & k\\ S & S' & S\end{Bmatrix} \tag{3.16}$$

where $\triangle B = B' - B$.

In principle B' and B are not exactly equal although in practice they do have a very similar value (13). Hence contributions from (3.10) with K odd and k even are expected to be very small indeed. Since $\triangle B$ is very small compared to B then these contributions will be of similar magnitude to the fourth order contributions. These even k, odd K terms will be returned to later.

The only significant terms remaining from (3.10) are hence those with both K and k odd. From table 1 it can be seen that only the terms with K = k = 1 come into this category. Substitution of these rank values into (3.10) leads to the following:

$$\langle \eta\Lambda S\Sigma J\Omega M \,|\, H^{(3)}_{SR}\,(K = k = 1)\,|\,\eta\Lambda S\Sigma'' J\Omega'' M\rangle =$$

$$-18\sum_{q'=\pm 1}^{\dagger}(-1)^{J-\Omega}\begin{pmatrix}J & 1 & J\\ -\Omega & q' & \Omega''\end{pmatrix}\left[J(J+1)(2J+1)\right]^{\frac{1}{2}}(-1)^{S-\Sigma}\begin{pmatrix}S & 1 & S\\ -\Sigma & q' & \Sigma''\end{pmatrix}$$

$$\times \sum_{\substack{\eta'\Lambda'S' \\ (q)}} (E^0_{\eta\Lambda S} - E^0_{\eta'\Lambda'S'})^{-2} (-1)^q (-1)^{S-\Sigma+S'-\Sigma} \begin{Bmatrix} 1 & 1 & 1 \\ S & S & S' \end{Bmatrix} \begin{pmatrix} 1 & 1 & 1 \\ q & -q-q' & q' \end{pmatrix}$$

$$\times \left| \langle \eta\Lambda S \| \sum_i T^1(\underline{s}_i)\, T^1_q(a_i \underline{l}_i) \| \eta'\Lambda'S' \rangle \right|^2 \Big\{ -B'[S'(S'+1)(2S'+1)]^{\frac{1}{2}}$$

$$\times \begin{Bmatrix} 1 & 1 & 1 \\ S & S' & S' \end{Bmatrix} \quad -B[S(S+1)(2S+1)]^{\frac{1}{2}} \begin{Bmatrix} 1 & 1 & 1 \\ S & S & S' \end{Bmatrix} \Big\} \tag{3.17}$$

Now from the orthogonality relations for the 3-j symbols it follows that

$$\sum_q \begin{pmatrix} 1 & 1 & 1 \\ q & -q-q' & q' \end{pmatrix}^2 = \frac{1}{3}$$

Thus

$$\sum_{q=\pm 1}^{\dagger} \begin{pmatrix} 1 & 1 & 1 \\ q & -q-q' & q' \end{pmatrix}^2 = \frac{1}{3} - \begin{pmatrix} 1 & 1 & 1 \\ 0 & -q' & q' \end{pmatrix}^2$$

$$= \frac{1}{3} - \frac{1}{6} = \frac{1}{6} = \begin{pmatrix} 1 & 1 & 1 \\ 0 & -q' & q' \end{pmatrix}^2$$

and so by substitution of this result and expansion of the 6-j symbols, (3.17) becomes equal to

$$+ \sum_{q'=\pm 1}^{\dagger} (-1)^{J-\Omega} \begin{pmatrix} J & 1 & J \\ -\Omega & q' & \Omega'' \end{pmatrix} [J(J+1)(2J+1)]^{\frac{1}{2}} (-1)^{S-\Sigma}$$

$$\times \begin{pmatrix} S & 1 & S \\ -\Sigma & q' & \Sigma'' \end{pmatrix} [S(S+1)(2S+1)]^{\frac{1}{2}} \Big\{ \sum_{\substack{\eta'\Lambda'S' \\ (q)}} (E^0_{\eta\Lambda S} - E^0_{\eta'\Lambda'S'})^{-2} (-1)^q$$

$$\times (-1)^{S-\Sigma+S'-\Sigma} \left| \langle \eta\Lambda S \| \sum_i T^1(\underline{s}_i) T^1_q(a_i \underline{l}_i) \| \eta'\Lambda'S' \rangle \right|^2$$

$$\times \left(\frac{S(S+1) - S'(S'+1) + 2}{(S+1)(2S+1)\, 4S} \right) [2(B+B') + (B'-B)(S(S+1) + S'(S'+1))] \Big\} \tag{3.18}$$

As has been noted, B and B' are very similar, so the term in square brackets is approximately equal to 2B. The term outside the braces in (3.18) is the matrix element of

$$\sum_{q'=\pm 1}^{\dagger} (-1)^{q'}\, T^1_{q'}(\underline{J})\, T^1_{-q'}(\underline{S})$$

and so (3.18) mimics the form of the spin-rotation interaction, the term within braces being the third-order contribution to the spin-rotation parameter γ. The operator equivalent form of this third-order term is identical to that in lower order and so to this order only a single γ parameter is required. Indeed, it has already been noted in the introduction to this chapter that γ_1 and γ_2 are found in practice to be the same, to within experimental error. There is thus both theoretical and practical justification for the use of a single spin-rotation parameter.

This is not to say, however, that Hougen's treatment is incorrect since in order to make any valid comparison the present treatment should be extended to all orders. In the next section the higher order forms of the spin-rotation interaction will be considered. The third order terms with k even and K odd have been estimated to be of the same magnitude as the fourth order contributions and for this reason will be considered in the next section.

3.4 Higher Order Spin-Rotation Interactions

From a general consideration of the form of equation (3.9) it can be seen that only terms with K odd contribute to the effective Hamiltonian. These terms can all be written in the operator equivalent form

$$T^0_0\ (\underline{J},\ \underline{S}^K)$$

i.e. the scalar product of a first rank $\underline{J}$ operator with a K^th^ rank $\underline{S}$ operator. Indeed, the usual method of writing the spin-rotation interaction

$$T^1\ (\underline{J}).\ T^1\ (\underline{S})$$

could just as easily be written as $T^0_0\ (\underline{J},\ \underline{S})$, the two forms differing only in a numerical factor. These results could also be obtained in an ad hoc manner by a consideration of time reversal. Under this operation, all the angular momenta reverse sign and hence if the Hamiltonian is to be invariant under time reversal then each interaction must contain an even number of angular momenta. Hence if K is even, the total number of angular momenta involved would be odd and so this type of term is expected to vanish. We can see therefore that for a $^4\Sigma$ state there will be contributions to the effective Hamiltonian from terms with K = 1 and with K = 3 and we would expect a determinable parameter from each of these. Hence Hougen's general conclusions about the number of spin-rotation parameters is in principle correct. The parameter associated with K = 1 is γ, the usual spin-rotation constant while that associated with $K = 3$ we have called γ_S for reasons mentioned later. This latter term has a contribution from the third order term with $K = 3$ and $k = 2$, which, as has already been mentioned, is approximately the same magnitude as a fourth order term, and for this reason was neglected in the previous section. The matrix elements of this operator are of the form

$$\langle \eta\Lambda;\ S\Sigma;\ J\Omega M \,|\, H_{SR}\ (K = 3) \,|\, \eta\Lambda;\ S\Sigma \pm 1;\ J\Omega \pm 1\ M \rangle$$

$$= -\tfrac{1}{2}\gamma_S [S(S+1) - 5\Sigma(\Sigma \pm 1) - 2]\,[J(J+1) - \Omega(\Omega \pm 1)]^{\frac{1}{2}}$$

$$\times\ [S(S+1) - \Sigma(\Sigma \pm 1)]^{\frac{1}{2}} \qquad (3.19)$$

Now the two square root expressions in (3.19) are the matrix elements of the usual spin-rotation interaction and so equation (3.19) mimics the form of the spin-rotation Hamiltonian, but with an effective parameter that is S and Σ dependent. It is thus apparent that the effective spin-rotation parameter will differ with Σ, and this is the origin of the difference between γ_1 and γ_2. By substitution of explicit S and Σ values for ${}^4\Sigma$ states the parameters γ_1 and γ_2 can be related to the more basic parameters γ and γ_S:

$$\gamma_1 = \gamma + 2\gamma_S$$

$$\gamma_2 = \gamma - 3\gamma_S \qquad (3.20)$$

or alternatively $\qquad \gamma_1 - \gamma_2 = 5\gamma_S$

By substitution of $k = 2$, $K = 3$ into (3.9) and expanding the 3-j symbol $\begin{pmatrix} S & 3 & S \\ -\Sigma & q' & \Sigma' \end{pmatrix}$ it can be seen by comparison with (3.19) that the third order contribution to γ_S is

$$\gamma_S = \frac{-70\sqrt{6}}{[(2S-2)(2S-1)(2S+3)(2S+4)]^{\frac{1}{2}}} \sum_{\substack{\eta'\Lambda'S' \\ (q)}} \left| \langle \eta\Lambda S \| \sum_i T^1(\underline{s}_i) T^1_q(a_i \underline{l}_i) \| \eta'\Lambda'S' \rangle \right|^2$$

$$\times\ (-1)^q\,(-1)^{S-\Sigma+S'-\Sigma}\,\Delta B\,(E^0_{\eta\Lambda S} - E^0_{\eta'\Lambda'S'})^{-2} \begin{pmatrix} 1 & 2 & 3 \\ q & -q\pm 1 & \mp 1 \end{pmatrix} \begin{pmatrix} 1 & 1 & 2 \\ -q & \pm 1 & q\mp 1 \end{pmatrix}$$

$$\times \begin{Bmatrix} 1 & 2 & 3 \\ S & S & S' \end{Bmatrix} \begin{Bmatrix} 1 & 1 & 2 \\ S' & S & S \end{Bmatrix} \qquad (3.21)$$

Table 2 presents the complete Hamiltonian matrix for levels in a $^4\Sigma$ state with a given J value. The 4 x 4 matrix is reduced to two 2 x 2 matrices, corresponding to e and f rotational levels (14, 15), by taking Wang sum and difference functions

$$|J, \Omega, \Sigma ; \pm\rangle = \frac{1}{\sqrt{2}}\left\{|J +\Omega +\Sigma\rangle \pm |J -\Omega -\Sigma\rangle\right\} \qquad (3.22)$$

Now for states of half-integral spin the e and f levels are defined (14, 15) as follows:

Levels with parity $+(-1)^{J-\frac{1}{2}}$ are e levels

Levels with parity $-(-1)^{J-\frac{1}{2}}$ are f levels

To make the correspondence between the e and f levels and the ± signs of (3.22) the parity of the wavefunctions in (3.22) has to be determined. By a consideration of how the Euler angles transform under the space fixed inversion (parity) operator E* it is found that these wavefunctions transform as follows:

$$E^*|\Lambda=0; J\Omega S\Sigma\rangle = \pm(-1)^{J-S}|\Lambda=0; J -\Omega\ S -\Sigma\rangle \qquad (3.23)$$

where the ± refers to $\Sigma^{\pm}$ states respectively.

Combining (3.22) and (3.23) the transformation of the Wang functions is obtained:

$$E^*|J\Omega S\Sigma ; \pm\rangle = \pm(-1)^{p}(-1)^{J-S}|J\Omega S\Sigma ; \pm\rangle \qquad (3.24)$$

where p is even for Σ^+ states and odd for Σ^- states. Hence for $^4\Sigma^+$ states, the ± signs in the Wang functions refer to states of parity $\mp(-1)^{J-\frac{1}{2}}$, the upper case referring therefore to f levels and the lower to e levels. For $^4\Sigma^-$ states this identity is reversed.

It is also possible to tie in the e and f labels with the F_i levels. For a $^4\Sigma$ rotational level there are four levels with a given J value, and these are labelled F_1, F_2, F_3 and F_4 with increasing energy. By going over to a case b) limit these F_i levels correspond to the N levels as follows

F_4 has $N = J + 3/2$
F_3 $N = J + 1/2$
F_2 $N = J - 1/2$
F_1 $N = J - 3/2$

Now the case b) levels of a $^4\Sigma^{\pm}$ state have parity

$$\pm(-1)^{N}$$

Table 2 Matrix representation of the effective rotational Hamiltonian of a $^4\Sigma$ state in a Wang basis.

	$\lvert J,3/2,\pm\rangle$	$\lvert J,1/2,\pm\rangle$
$\langle J,3/2,\pm\rvert$	$B(J-1/2)(J+3/2)$ $-D[(J-1/2)^2(J+3/2)^2+3(J-1/2)(J+3/2)]$ $+2[\lambda+2\lambda_J(J-1/2)(J+3/2)]$ $-[\gamma+2\gamma_J(J-1/2)(J+3/2)]$	$-[3(J-1/2)(J+3/2)]^{1/2}$ $x[B-\gamma/2-\gamma_S-\{(J-1/2)(J+3/2)+7\}\gamma_J/2$ $-2D\{(J-1/2)(J+3/2)+2\}\pm(2D+\gamma_J)(J+1/2)]$
$\langle J,1/2,\pm\rvert$		$B[(J-1/2)(J+3/2)+4]$ $-D[\{(J-1/2)(J+3/2)+4\}^2+7(J-1/2)(J+3/2)+4]$ $-2[\lambda+2\lambda_J\{(J-1/2)(J+3/2)+4\}]$ $-[\gamma+2\gamma_J\{(J-1/2)(J+3/2)+9/4\}]7/2$ $\mp2[B-\gamma/2+3\gamma_S/2-\gamma_J\{(J-1/2)(J+3/2)+11\}/2$ $-2D\{(J-1/2)(J+3/2)+4\}-4\lambda_J](J+1/2)$

so we can see that F_2 and F_4 levels have the same parity, which is the opposite parity to F_1 and F_3 levels. An F_2 level of a $^4\Sigma^+$ state therefore has parity $(-1)^{J-\frac{1}{2}}$ and so corresponds to an <u>e</u> level. Therefore for $^4\Sigma^+$ states

F_1 and F_3 levels are <u>e</u> levels
F_2 and F_4 levels are <u>f</u> levels

while for $^4\Sigma^-$ states the <u>e</u> and <u>f</u> labels are reversed.

The matrix elements given in table 2 are consistent with those of Martin and Merer (9) except that their definitions of γ_1 and γ_2 do not agree with the present ones. This is because they have not renormalised the second order wavefunction. Hougen (6) has also not included this in his treatment. If this renormalisation is performed then the γ_1 and γ_2 parameters defined in these papers become the same, to third order. Martin and Merer's γ_1 and γ_2 differ only in the admixture of $^2\Sigma$ states, so we shall assume for the present that the $^4\Sigma$ state is contaminated by a single $^2\Sigma$ state only. Hougen gives the normalised wavefunctions for $^4\Sigma$ states as follows, in terms of kets $|^{2S+1}\eta;\Lambda,\Sigma\rangle$

$$|^4\Sigma_{-3/2}\rangle = a_2\,|^4\Sigma;\ 0,\ -3/2\rangle + b_2\,|^4\Pi;\ -1,\ -1/2\rangle$$

$$|^4\Sigma_{-1/2}\rangle = a_1\,|^4\Sigma;\ 0,\ -1/2\rangle + b_1\,|^4\Pi;\ -1,\ 1/2\rangle$$
$$+ c\,|^4\Pi;\ 1,\ -3/2\rangle + d\,|^2\Sigma;\ 0,\ -1/2\rangle$$

$$|^4\Sigma_{1/2}\rangle = a_1\,|^4\Sigma;\ 0,\ 1/2\rangle + b_1\,|^4\Pi;\ 1,\ -1/2\rangle$$
$$+ c\,|^4\Pi;\ -1,\ 3/2\rangle + d\,|^2\Sigma;\ 0,\ 1/2\rangle$$

$$|^4\Sigma_{3/2}\rangle = a_2\,|^4\Sigma;\ 0,\ -3/2\rangle + b_2\,|^4\Pi;\ 1,\ 1/2\rangle \tag{3.25}$$

Hence if only a single $^2\Sigma$ state perturbs the $^4\Sigma$ wavefunctions we have

$$|^4\Sigma_{\pm 3/2}\rangle = a_2\,|^4\Sigma;\ 0,\ \pm 3/2\rangle$$

$$|^4\Sigma_{\pm 1/2}\rangle = a_1\,|^4\Sigma;\ 0,\ \pm 1/2\rangle + d\,|^2\Sigma;\ 0,\ \pm 1/2\rangle \tag{3.26}$$

which on renormalisation gives

$$a_2 = 1$$
$$a_1 = \sqrt{1 - d^2} \qquad (3.27)$$

By substitution of (3.26) and (3.27) into Hougen's definitions for the γ_1 and γ_2 matrix elements, (3.2) and (3.3), we obtain:

$$\langle J\Omega=3/2|H_{SR}|J\Omega=1/2\rangle = 1-d^2 \langle {}^4\Sigma;\ J\ 3/2|H_{SR}|{}^4\Sigma;\ J\ 1/2\rangle \qquad (3.28)$$

and
$$\langle J\Omega=1/2|H_{SR}|J\Omega=-1/2\rangle = a_1^2\langle {}^4\Sigma;\ J\ 1/2|H_{SR}|{}^4\Sigma;\ J\ -1/2\rangle$$
$$+ d^2\langle {}^2\Sigma;\ J\ 1/2|H_{SR}|{}^2\Sigma;\ J\ -1/2\rangle \qquad (3.29)$$
$$= (1 - \tfrac{1}{2}d^2)\langle {}^4\Sigma;\ J\ 1/2|H_{SR}|{}^4\Sigma;\ J\ -1/2\rangle$$

since $\langle {}^2\Sigma;\ 1/2|\ |{}^2\Sigma;\ -1/2\rangle = 1/2\langle {}^4\Sigma;\ 1/2|\ |{}^4\Sigma;\ -1/2\rangle$ and using equation (3.25). By expanding the square root in (3.28) and neglecting terms of order d^4 or higher, the ratio of (3.28) and (3.29) gives

$$\frac{\langle J\ 3/2|H_{SR}|J\ 1/2\rangle}{\langle J\ 1/2|H_{SR}|J\ -1/2\rangle} = \frac{\langle {}^4\Sigma;\ J\ 3/2|H_{SR}|{}^4\Sigma;\ J\ 1/2\rangle}{\langle {}^4\Sigma;\ J\ 1/2|H_{SR}|{}^4\Sigma;\ J\ -1/2\rangle} \qquad (3.30)$$

and hence to this order $\gamma_1 = \gamma_2$.

Note also that the spin-splitting of the fine structure states given in table 2 is 4λ, as suggested by Martin and Merer (9), rather than 6λ as used by Hougen (6). The use of 4λ is consistent with the form of the spin-spin interaction given in equation (2.56) of chapter 2. Centrifugal distortion corrections to B, λ and γ are also included, the parameters describing these being D, λ_J and γ_J respectively. The K = 3 spin-rotation parameter is labelled γ_S by analogy with these centrifugal distortion parameters.

Since γ_S is very small, the approximate order of magnitude being $\frac{JA^2\Delta B}{(\Delta E)^2}$, then to a fairly high degree of approximation $\gamma_1 = \gamma_2 = \gamma$. Two or more spin-rotation parameters therefore will only be required if the experimental precision permits the detection of terms of the order of γ_S. In the case of optical work, which has a resolution of $\sim 0.05\text{cm}^{-1}$, the detection of such terms might be possible for a heavy element hydride, particularly in very high rotational levels, since for such radicals both B and A are large. In addition we note that the triangle rules on $\begin{Bmatrix} 1 & 2 & 3 \\ S & S & S' \end{Bmatrix}$ mean that such terms will only arise in states with spin S $3/2$, i.e. only for states of quartet or higher multiplicity. By appealing to higher orders of perturbation theory it can be seen that, in principle, further spin-rotation parameters arise. For instance in fifth order an interaction of form $T^0_0(\underline{J}, \underline{S}^5)$ is expected to arise but since this will be very much smaller than even the γ_S term then it will be essentially undetectable. This term would apply only to states of sextet or higher multiplicity and is in principle responsible for the third spin rotation parameter needed for such states.

3.5 Spin-Spin Interactions in Σ States of Quintet and Higher Multiplicity

In the previous sections we have shown how Hougen's general conclusions about the number of parameters needed to describe spin-interactions in molecules in Σ states are in principle correct, though in practice the number of determinable parameters, which is governed by the experimental precision, may be less than predicted. In addition we have shown how the higher-order spin-dependent terms in the effective Hamiltonian can be cast into operator equivalent form, and how by use of the triangle rules on the Wigner n-j symbols we can determine what ranks of tensor interactions arise for a state of given multiplicity. In general, a contracted tensor spin operator of rank K will only arise in states of multiplicity greater than or equal to K + 1. For example $T^0_0(\underline{J}, \underline{S}^3)$ interactions, with $K = 3$, do not occur in states of less than quartet multiplicity. Similarly the fourth rank spin-spin interaction is not expected to arise in states of less than quintet multiplicity. There has been a growing interest in high multiplicity states of transition metal and rare-earth diatomic oxides (16, 17) and it is in heavy diatomics that such higher order spin-spin interactions would be expected to be detectable. For this reason, the form of this fourth rank term has been investigated further. In addition, since Hougen predicts that for quintet states two spin-spin parameters would be required, this fourth rank term is expected to be responsible for the additional parameter.

The second rank spin-spin interaction operator $T^2_0(\underline{S}, \underline{S})$ was discussed in chapter 2, where it was shown that the second order perturbation terms arising from states mixed in solely by spin-orbit coupling, mimic the form of the first order spin-spin interaction. Similarly in third-order of perturbation theory, contributions to this second rank term are expected but by a brief consideration of whether the total number of angular momenta involved is odd or even it can be seen that no new terms arise. In fourth order, however, a similar consideration reveals that a fourth rank tensor contraction of four spin angular momenta can be obtained, in addition to the usual second rank term. The general fourth-order effective Hamiltonian is given in equation (2.24) of chapter 2. If the perturbation V is taken to be the spin-orbit coupling operator then the only terms that give rise to an effective spin-spin interaction in a Σ state are

$$\begin{aligned}(P_0VU)_4 \;=\; & P_0V\,(Q_0/a)\,V\,(Q_0/a)\,V\,(Q_0/a)\,VP_0 \\ & - P_0V\,(Q_0/a^2)\,VP_0V\,(Q_0/a)\,VP_0 \qquad (3.31)\end{aligned}$$

since all the other terms involve matrix elements of the spin-orbit operator within a Σ state and hence are zero. Examples of such non-zero contributions are illustrated in figure 5 in the form of 'railroad' diagrams.

Four matrix elements of the spin-orbit interaction are involved in each of these fourth order terms, and hence there are four 3-j symbols in each. As described in section 3.2 of this chapter, these 3-j symbols can be contracted to give 6-j symbols by use of equation (2.39) of chapter 2. In this case however there will be three contractions and hence three tensor ranks k_1, k_2 and K resulting from these successive contractions. The details of this calculation need not be repeated, so just the final result is quoted. The following diagonal matrix element is obtained:

$$\langle \eta\Lambda;\, S\Sigma;\, J\Omega M \,|\, H^{(4)}_{\mathrm{eff}} \,|\, \eta\Lambda;\, S\Sigma;\, J\Omega M \rangle$$

$$= \sum_{\eta_1\Lambda_1} \sum_{\eta_2\Lambda_2} \sum_{\eta_3\Lambda_3} \left(E^0_{\eta\Lambda S} - E^0_{\eta_1\Lambda_1S_1}\right)^{-1} \left(E^0_{\eta\Lambda S} - E^0_{\eta_3\Lambda_3S_3}\right)^{-1}$$

$$\times \langle \eta\Lambda S \| \sum_i T^1(\underline{s}_i) T^1_{q_1}(a_i \underline{l}_i) \| \eta_1\Lambda_1S_1 \rangle \langle \eta_3\Lambda_3S_3 \| \sum_i T^1(\underline{s}_i) T^1_{q_4}(a_i \underline{l}_i) \| \eta\Lambda S \rangle$$

$$\times \sum_K (-1)^K\,(2K+1)\,(-1)^{S-\Sigma} \begin{pmatrix} S & K & S \\ -\Sigma & 0 & \Sigma \end{pmatrix} \sum_{k_1,\,k_2} (2k_1+1)(2k_2+1)$$

$$\times \left\{ \left[\begin{Bmatrix} 1 & 1 & k_1 \\ S_2 & S & S_1 \end{Bmatrix} \begin{Bmatrix} k_1 & 1 & k_2 \\ S_3 & S & S_2 \end{Bmatrix} \begin{Bmatrix} k_2 & 1 & K \\ S & S & S_3 \end{Bmatrix} \begin{pmatrix} 1 & 1 & k_1 \\ -q_1 & -q_2 & q_1+q_2 \end{pmatrix} \begin{pmatrix} 1 & k_1 & k_2 \\ q_3 & q_1+q_2 & q_4 \end{pmatrix} \right.\right.$$

$$\times \begin{pmatrix} 1 & k_2 & K \\ q_4 & -q_4 & 0 \end{pmatrix} \left(E^0_{\eta\Lambda S} - E^0_{\eta_2\Lambda_2S_2}\right)^{-1} (-1)^{S_1+S_2+q_3}$$

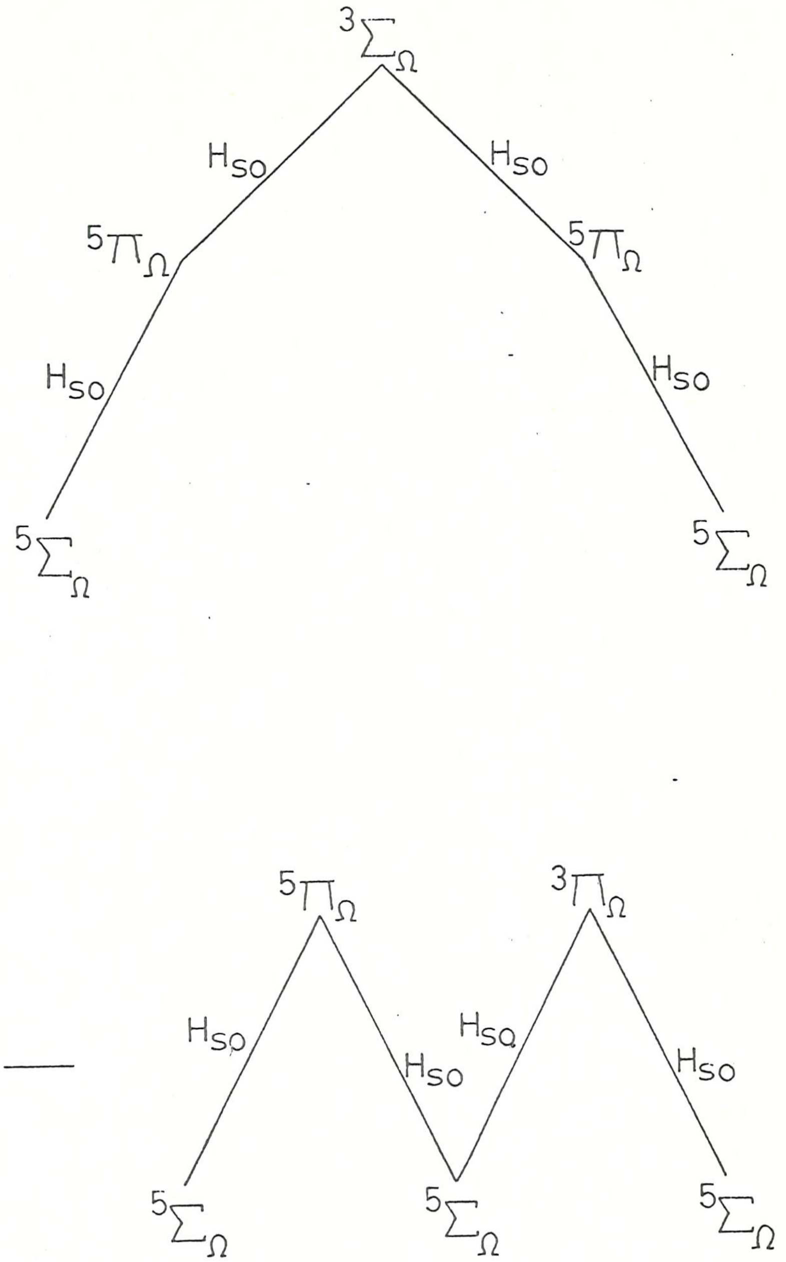


Figure 5 Some fourth-order contributions to the spin-spin interaction in a $^5\Sigma$ state.

Note that all the matrix elements are diagonal in Ω.

$$\times \langle \eta_1\Lambda_1 S_1 \| \sum_i T^1(\underline{s}_i)T^1_{q_2}(a_i\underline{l}_i) \| \eta_2\Lambda_2 S_2\rangle \langle \eta_2\Lambda_2 S_2 \| \sum_i T^1(\underline{s}_i)T^1_{q_3}(a_i\underline{l}_i) \| \eta_3\Lambda_3 S_3 \rangle \Big]$$

$$- \left[\begin{Bmatrix} 1 & 1 & k_1 \\ S & S & S_1 \end{Bmatrix} \begin{Bmatrix} k_1 & 1 & k_2 \\ S_3 & S & S \end{Bmatrix} \begin{Bmatrix} k_2 & 1 & K \\ S & S & S_3 \end{Bmatrix} \begin{pmatrix} 1 & 1 & k_1 \\ -q_1 & q_1 & 0 \end{pmatrix} \right.$$

$$\times \begin{pmatrix} 1 & k_1 & k_2 \\ -q_4 & 0 & q_4 \end{pmatrix} \begin{pmatrix} k_2 & 1 & K \\ q_4 & -q_4 & 0 \end{pmatrix} (-1)^{S+S_3-q_4} \left(E^0_{\eta\Lambda S} - E^0_{\eta_1\Lambda_1 S_1}\right)^{-1}$$

$$\left. \times \langle \eta_1\Lambda_1 S_1 \| \sum_i T^1(\underline{s}_i)T^1_{-q_1}(a_i\underline{l}_i) \| \eta\Lambda S\rangle \langle \eta\Lambda S \| \sum_i T^1(\underline{s}_i)T^1_{-q_4}(a_i\underline{l}_i) \| \eta_3\Lambda_3 S_3 \rangle \right]\Bigg\} \qquad (3.32)$$

where q_1, q_2, q_3, q_4 are the components of each of the individual spin-orbit terms. These can take the values 0, ± 1, subject to the restriction

$$q_1 + q_2 + q_3 + q_4 = 0 \qquad (3.33)$$

The labels used for the quantum numbers in (3.32) have the significance shown in figure 6. The values that k_1, k_2 and K are allowed to take are governed by the triangle rules on the Wigner symbols and are shown in table 3.

Expression (3.32) is even more unwieldy than the third order terms but fortunately the general results can be obtained without performing any further simplifications. From the properties of 3-j symbols, it is easily seen that (3.32) vanishes for K odd if <u>all</u> the q values are zero. Similarly, as was done with the lower order terms, an examination of the effect of replacing +q components by their negatives reveals that, for Σ states only, the above expression is multiplied by a phase factor of $(-1)^K$ on making this substitution. Thus for odd K values the expression for +q is equal in magnitude but opposite in sign to that for -q, and so the summation over q = ± 1 gives no net contribution to (3.32). Hence the only non-zero contributions to (3.32) are those with K even.

Equation (3.32) can be reexpressed in operator equivalent form as

$$\langle \eta\Lambda ; S\Sigma | H^{(4)}_{eff} | \eta\Lambda ; S\Sigma \rangle =$$

$$(-1)^{S-\Sigma} \sum_K \begin{pmatrix} S & K & S \\ -\Sigma & 0 & \Sigma \end{pmatrix} \langle S \| T^K(\underline{S}) \| S \rangle \, T^K_0(\lambda) \qquad (3.34)$$

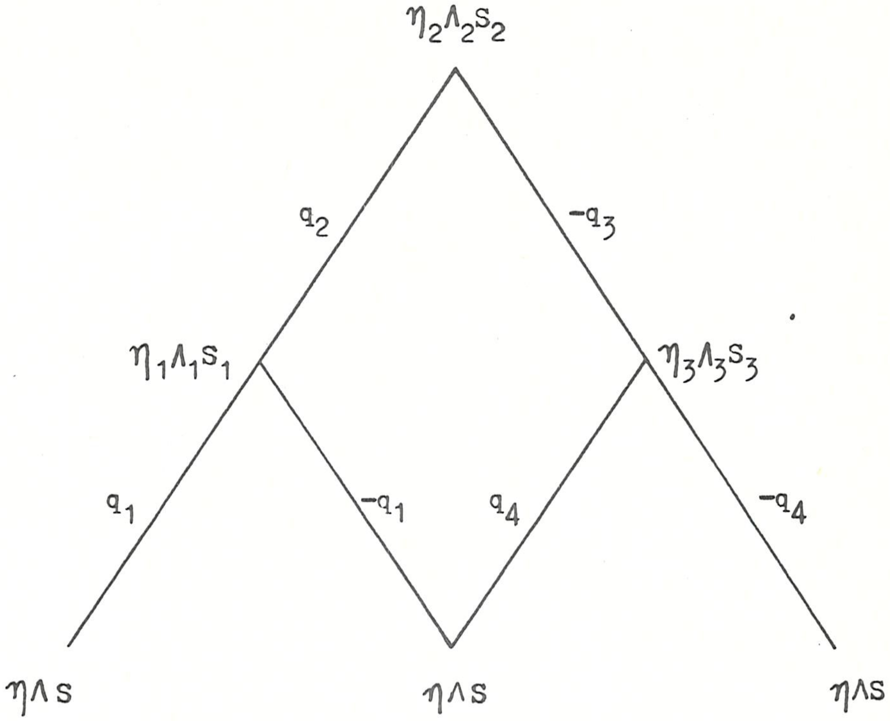


Figure 6 Notation used in calculation of fourth-order spin-spin interactions.

k_1	k_2	K
0	1	0,1,2
1	0	1
	1	0,1,2
	2	1,2,3
2	1	0,1,2
	2	1,2,3
	3	2,3,4

Table 3 Allowed values for the tensor ranks k_1, k_2 and K in the calculation of fourth-order contributions to the spin-spin interaction.

which are just the matrix elements of the K^{th} rank spin-spin interaction, where K can take the values 0, 2 and 4. The reduced matrix element $\langle S \| T^K(\underline{S}) \| S \rangle$ does not appear explicitly in equation (3.32) but this can be extracted quite easily, either by expanding the 6-j symbols or by simultaneously multiplying and dividing by this factor, in which case the reciprocal has to be incorporated in the parameter $T_0^K(\lambda)$. Note that the rotational quantum numbers J, Ω and M have been suppressed from the molecular wavefunction in (3.34) since this particular fourth order Hamiltonian does not operate on the rotational coordinates.

As discussed in chapter 2, the term with K = 0 is a scalar quantity which can be absorbed into the electronic origin, while the K = 2 term is just a further contribution to the usual spin-spin parameter λ (or $T_0^2(\lambda)$). The term with K = 4 however has not been needed for the multiplicities we have discussed so far. From the triangle rules on $\begin{pmatrix} S & 4 & S \\ -\Sigma & 0 & \Sigma \end{pmatrix}$ the restriction $2S \geqslant 4$ is obtained, and so the parameter $T_0^4(\lambda)$ will only be needed for states of quintet and higher multiplicity, as was predicted from more general arguments. The contribution due to this term is therefore obtained by substitution of K = 4 into (3.34) but as the reduced matrix element and 3-j symbol thus obtained are not quoted in any of the standard texts on angular momentum, we give some indication of their derivation. The 3-j symbol can be calculated by a standard recursive procedure from 3-j symbols of lower tensor rank and as such fourth rank 3-j symbols have already been tabulated (18) we merely quote the result:

$$\begin{pmatrix} S & 4 & S \\ -\Sigma & 0 & \Sigma \end{pmatrix} = (-1)^{S-\Sigma} \frac{2[35\Sigma^4 - 30S(S+1)\Sigma^2 + 25\Sigma^2 - 6S(S+1) + 3S^2(S+1)^2]}{[(2S-3)(2S-2)(2S-1)2S(2S+1)(2S+2)(2S+3)(2S+4)(2S+5)]^{\frac{1}{2}}} \tag{3.35}$$

The reduced matrix element is rather more difficult to evaluate. The fourth rank tensor operator can be reexpressed in terms of second rank tensor operators by using standard relations, to obtain the following:

$$T_0^4(\underline{S}) = \sum_q T_q^2(\underline{S})\, T_{-q}^2(S) \times 3 \begin{pmatrix} 2 & 2 & 4 \\ q & -q & 0 \end{pmatrix} \tag{3.36}$$

where q can take the values q = 0, ±1, ±2. By expansion of the 3-j symbol in (3.36) for each of these q values we obtain

$$T_0^4(\underline{S}) = \frac{1}{\sqrt{70}} \left[T_2^2(\underline{S})\, T_{-2}^2(\underline{S}) + 4T_1^2(\underline{S})\, T_{-1}^2(\underline{S}) + 6T_0^2(\underline{S})\, T_0^2(\underline{S}) + 4T_{-1}^2(\underline{S})\, T_1^2(\underline{S}) + T_{-2}^2(\underline{S})\, T_2^2(\underline{S}) \right] \tag{3.37}$$

The matrix elements $\langle S\Sigma | T^4_0(\underline{S}) | S\Sigma \rangle$ are sought after, but as (3.34) must hold for <u>any</u> value of Σ then the problem can be simplified by setting $\Sigma = S$. Hence

$$\begin{aligned}\langle SS | T^4_0(\underline{S}) | SS \rangle = \frac{1}{\sqrt{70}} \Big[& \langle SS | T^2_2(\underline{S}) | SS-2 \rangle \langle SS-2 | T^2_{-2}(\underline{S}) | SS \rangle \\ + & \langle SS | T^2_1(\underline{S}) | SS-1 \rangle \langle SS-1 | T^2_{-1}(\underline{S}) | SS \rangle \\ + & \langle SS | T^2_0(\underline{S}) | SS \rangle \langle SS | T^2_0(\underline{S}) | SS \rangle \\ + & \langle SS | T^2_{-1}(\underline{S}) | SS+1 \rangle \langle SS+1 | T^2_1(\underline{S}) | SS \rangle \\ + & \langle SS | T^2_{-2}(\underline{S}) | SS+2 \rangle \langle SS+2 | T^2_2(\underline{S}) | SS \rangle \Big] \qquad (3.38)\end{aligned}$$

The final two terms in (3.38) are zero since the components ($\Sigma = S+1$ or $S+2$) are greater than the rank S. By expansion of the matrix elements in (3.38) the following expression is obtained:

$$\begin{aligned}\langle SS | T^4_0(\underline{S}) | SS \rangle &= \frac{|\langle S \| T^2(\underline{S}) \| S \rangle|^2}{\sqrt{70}} \\ &\times \left\{ \begin{pmatrix} S & S & 2 \\ S-2 & -S & 2 \end{pmatrix}^2 - 4 \begin{pmatrix} S & S & 2 \\ S-1 & -S & 1 \end{pmatrix}^2 + 6 \begin{pmatrix} S & S & 2 \\ S & -S & 0 \end{pmatrix}^2 \right\} \\ &= \frac{2S(2S-1)(2S-2)(2S-3)}{4\sqrt{70}} \qquad (3.39)\end{aligned}$$

But the relation

$$\langle SS | T^4_0(\underline{S}) | SS \rangle = \begin{pmatrix} S & 4 & S \\ -S & 0 & S \end{pmatrix} \langle S \| T^4(\underline{S}) \| S \rangle \qquad (3.40)$$

also holds, which by comparison with (3.39) and evaluation of the 3-j symbol by use of (3.35) leads to the required reduced matrix element

$$\langle S \| T^4(\underline{S}) \| S \rangle = \frac{1}{4\sqrt{70}} \left[(2S-3)(2S-2)(2S-1)2S(2S+1)(2S+2)(2S+3)(2S+4)(2S+5) \right]^{\frac{1}{2}} \qquad (3.41)$$

The fourth order contribution to $T_0^4(\lambda)$ can now be obtained from equation (3.32) by substitution of $k_1 = 2$, $k_2 = 3$ and $K = 4$. There is, as far as we know, no experimental evidence for this fourth rank term for a linear molecule. Its effects are approximately proportional to $\frac{A^4}{(\Delta E)^3}$ which is likely to be extremely small ($\sim 0.001 cm^{-1}$) unless a heavy atom is present in the molecule, so that the spin-orbit coupling constant is large. Fourth rank spin-spin terms have been detected in the ESR spectra of transition metal ions that are trapped in cylindrically symmetric environments (19) and the constants that are obtained are of similar magnitude to those estimated in this chapter.

Finally we note that this fourth rank term could be written as a second rank interaction, but with Σ dependent parameters. Thus the total interaction could be described only in terms of a second rank spin-spin interaction, using several λ values to allow for the Σ dependence of the parameters. This is consistent with Hougen's general conclusions about the number of spin-spin parameters that are required. A simple parametric dependence between the λ_i's and $T_0^K(\lambda)$ is thus anticipated, but since the $T_0^K(\lambda)$ with $K \geqslant 4$ are likely to be extremely small then the λ_i's are expected to be the same to within experimental error, using present techniques.

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CHAPTER 4

GAS PHASE ELECTRON PARAMAGNETIC RESONANCE SPECTROSCOPY

In this chapter we shall consider some of the general principles of gas phase e.p.r. spectroscopy. Some of the details presented here will be of relevance in the two following chapters.

4.1 Comparison with Ordinary Microwave Spectroscopy

In order to describe this technique it would perhaps be of benefit to describe the simpler, closely related method of pure microwave absorption spectroscopy. The separations between successive rotational energy levels correspond, with a few exceptions, to energies in the microwave region, the exceptions being for extremely light molecules such as OH and OD where the spacing between levels is much greater and falls in the far infrared. We shall ignore such exceptions in what follows. If a gaseous sample is irradiated with microwave radiation over a range of frequencies, absorption of radiation at certain specific frequencies will occur, these absorptions resulting when the energy of the incident radiation exactly matches the energy separation of a pair of rotational levels so that a transition is induced from the lower level to the upper with accompanying absorption of radiation. The principle of a pure microwave absorption experiment is to sweep the incident microwave frequency and to detect the absorption of radiation as a function of this frequency. By identifying the levels between which the transition occurs, information on the disposition of the energy levels can be obtained.

In contrast to the above technique, an e.p.r. spectrometer operates at a single, fixed microwave frequency and the separation between energy levels is tuned to this frequency by application of an external magnetic field. The reason the energy levels are tunable in this manner requires some further explanation. In the absence of nuclear spins within the molecule, the energy levels can be labelled by two quantum numbers J and m_J, where m_J takes the (2J + 1) values

$$m_J = J, J - 1 \ldots, - J$$

Other quantum numbers are required to define the energy levels completely, as discussed in chapter 2, but these need not be considered here. In the absence of external magnetic or electric fields, levels with the same value of J are (2J + 1)-fold degenerate, that is to say the (2J + 1) states

$|J\ m_J\rangle$ have the same energy. On application of an external magnetic field this degeneracy is lifted, each rotational level being split into (2J + 1) levels corresponding to the different m_J values. This is the well-known Zeeman effect. The splittings between the states $|J\ m_J\rangle$ depend on the magnitude of the magnetic flux density, and on the effective magnetic moments for such states. Each of the m_J levels therefore tunes with magnetic field at a different rate.

If we consider a pair of m_J levels correlating with different J values, their energy separation can be seen to be a function of the applied magnetic field. Thus if the magnetic field is swept it is possible that at a certain value of the magnetic flux density, the energy separation of these levels coincides with the (fixed) energy of the incident microwave radiation, so that absorption of radiation takes place. This is the basis of e.p.r. spectroscopy: the absorption is measured as a function of magnetic flux density, the lines observed in this manner corresponding to different pairs of energy levels being brought into resonance with the fixed frequency at which the spectrometer operates.

This type of experiment gives similar information to the pure microwave absorption experiments but gives additional information on the magnetic moments within the molecule. There are further differnces too. Since it is necessary to have a substantial magnetic moment before the energy levels can be tuned with any rapidity it is apparent that only species endowed with a sizeable paramagnetism (such as most free radicals) can be successfully observed by this technique. In principle the pure microwave absorption technique is applicable to both free radicals and stable closed-shell molecules although in practice the former are quite difficult to observe. The reason for this lies partly in the nature of the experimental arrangement and partly in the instability of the free radicals. The absorption cell used in ordinary microwave spectroscopy is either a length of waveguide or a length of glass tube along which the sample is passed. This cell has to be capable of transmitting microwave radiation over a range of frequencies. The sensitivity of such a system is proportional to the length of the absorption cell, amongst other factors, but if a cell is made longer, so as to improve sensitivity, the problem arises of how to fill the cell with radicals, since they are so short-lived.

Such problems do not arise in the case of e.p.r. spectroscopy. Since a single fixed frequency is used it is possible to use a resonant cavity as the absorption cell. These cavities resonate at certain frequencies determined by its geometry. It is therefore possible to build such a cavity that resonates at the operating frequency of the spectrometer. These resonant cavities have several advantages over the absorption cells used in ordinary microwave experiments. First, their internal volume tends to be very small, typically $\sim 30\text{cm}^3$ for one operating at X-band frequencies, and so there is not such a great problem in filling them with radicals. Secondly, because these cavities store energy at their resonant frequencies, radicals passing through the cavity are subjected to more intense radiation fields and consequently the sensitivity of the system is much greater. Maximum sensitivity occurs when power saturation of the sample is just reached and it is much easier to achieve this condition using a resonant cavity system. Typical linewidths for both types of microwave experiment are in the range 10kHz - 1MHz, the dominant contribution to these linewidths being pressure broadening. However, since frequencies can be measured more accurately than magnetic fields, the conventional microwave methods lead to more accurate parameters. With regard to searching for spectra from new radicals, the e.p.r. method is of more value, because magnetic moments can be estimated more readily than can rotational constants, and so the search problem is not so great.

High resolution studies can be performed using other techniques, such as molecular beam methods, but we shall not deal with these. It is sufficient to point out that the linewidths obtainable in a molecular beam study are very much narrower than in the above microwave techniques, being typically in the range 100Hz to 10kHz.

In the next section some typical types of resonant cavity, such as used in e.p.r. experiments, are discussed.

4.2 Cells for e.p.r. Studies

There are two basic types of cell that can be used in e.p.r. experiments, microwave cavities and Fabry-Perot resonant cells. We shall discuss each of these in turn, paying particular attention to the latter since this is the type used in the detection of OH, described in the following chapter, and because it has only recently come into use it has not to our knowledge been described in the literature of e.p.r. studies.

Microwave Cavities

These can be further classified into transmission or reflection types, depending respectively on whether the radiation passes straight through the cavity, being coupled out at the opposite end to which it is coupled in, or or whether a single iris doubles as both input and output coupling iris.

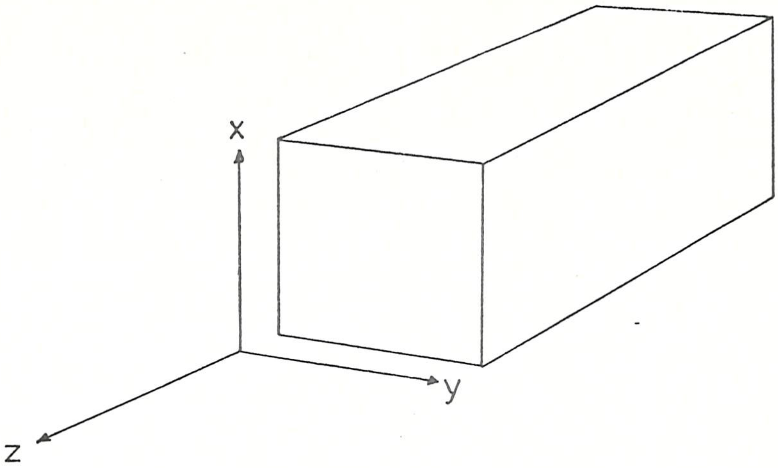
The latter is the type used most frequently for e.p.r. studies. Both types are described quite thoroughly by Poole (1). They consist of a cylindrical or parallelepipedal shaped space enclosed within walls of high conductivity metal, such as brass, copper, silver or gold. These are commonly known as cylindrical and rectangular cavities respectively.

The walls of the cavity reflect the radiation entering through the coupling iris and at certain frequencies a standing wave can result from constructive interference of the reflections. The metal walls transmit a small amount of radiation, a measure of this being the skin depth δ , which is defined as the depth at which the current density is $\frac{1}{e}$ times that on the surface. The skin depth is of the order of 0.01mm for microwave radiation of about 10GHz and hence it is not necessary to construct the entire cavity from expensive metals such as gold or silver - a thin coating on the surface of a much cheaper material will suffice. Several different standing waves, or modes, can be supported by a given cavity and these are classified as TE_{mnp} or TM_{mnp} modes. The subscripts m, n and p refer to the numbers of half-wavelength variations along the three axes of the cavity. For a rectangular cavity these refer respectively to the x, y and z axes whereas for a cylindrical cavity they refer to ϕ , r and z axes respectively. These two axis systems are defined in figure 1. TE and TM stand for "transverse electric" and "transverse magnetic" respectively, which means that the component of either the electric or the magnetic vectors of the radiation supported in the cavity along the z axis is zero respectively. The frequency of the radiation supported in these modes is a function of the dimensions of the cavity and of the mode numbers m, n and p. In general, as the dimensions of the cavity are decreased so the frequency of the resonant modes is increased.

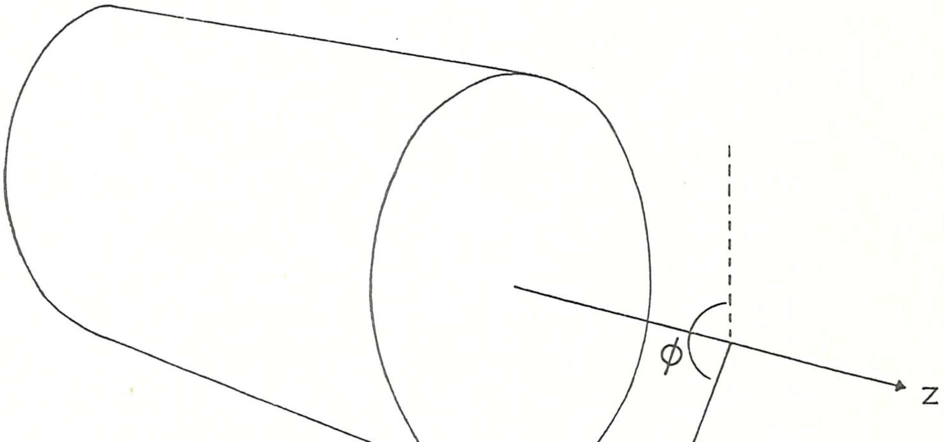
For use in gas phase e.p.r. spectroscopy these cavities form an integral part of the gas flow system and so it is necessary to drill inlet and outlet ports through the metal walls. This results in some loss of microwave ports but by judicious positioning of the holes, and provided they are not too large, these losses can be kept to a minimum.

A measure of losses in resonant cavities is the so-called Q-factor, or quality factor, which is inversely proportional to the total energy loss, contributions to the total loss arising from, for instance, losses through the cavity walls, through gas ports, coupling irises, and from dielectric losses through the medium. It is important that the Q-factor is as high as possible. Since the Q-factor has the alternative definition

Figure 1 Coordinate systems for rectangular and cylindrical cavities.



Rectangular coordinates



Cylindrical coordinates

$$Q = \nu/\Delta\nu$$

where ν is the resonant frequency

$\Delta\nu$ is the bandwidth of the cavity,

then a large Q means a narrow bandwidth. The detection system requires the operating frequency of the spectrometer to be very close to the resonant frequency of the cavity for optimum sensitivity and in practice this is achieved by locking the source frequency to that of the cavity. A narrow bandwidth means that, once locked, the two frequencies remain extremely close together, which improves the sensitivity of the system. The square root of the Q-factor is a measure of the signal-to-noise ratio obtainable. Typical Q-factors for microwave resonant cavities are 5000 to 10000.

The rectangular cavities have been used most often in the study of condensed phases by electron spin resonance, a very similar experimental technique to e.p.r., whereas for gas phase studies the cylindrical cavities are generally used. Two types of cylindrical cavity have been developed specifically for the study of gas phase species, one with its cylinder axis parallel to the direction of applied magnetic field and the other with its axis perpendicular. The former, such as developed by Carrington and Hyde and described by Carrington, Levy and Miller (2), operates in a TE_{01p} mode and can be used for experiments using either Zeeman or Stark modulation. Because the component of the electric vector lies perpendicular to the magnetic field this system can be used to study $\Delta m_J = \pm 1$ electric dipole transitions. The magnetic vector is orientated parallel to the external magnetic field and so $\Delta m_J = 0$ magnetic dipole transitions can also be studied.

The second type similarly operates in a TE_{01p} mode but it is not possible to use Stark modulation with it. In this case the ports are drilled through the flat ends of the cylinder and it is possible to make them much larger than for the previous type, without decreasing the Q-factor significantly. Consequently this type will be referred to as a 'wide access' cavity. This was the type used by Radford (3) in the first ever gas phase e.p.r. experiments on unstable molecular radicals. The magnetic vector in the modes supported by this cavity lies perpendicular to the magnetic field so $\Delta m_J = \pm 1$ magnetic dipole transitions can be observed, whereas the electric vector lies in both perpendicular and parallel orientations in different parts of the cavity, so both $\Delta m_J = 0$ and $\Delta m_J = \pm 1$ electric dipole transitions can be studied.

Fabry-Perot Resonators

As has been mentioned already, as the dimensions of a reflection cavity are decreased so the frequencies of its resonant modes increase. For example, at frequencies around 9GHz the internal volume of a reflection cavity operating in a TE_{011} mode is about $30cm^3$. For a similar cavity with a resonant frequency of about 80GHz, the internal volume is about $0.1cm^3$ which is certainly far too small to be of any practical use for free radical studies. One solution is to use higher order modes, in this case modes such as TE_{012} or TE_{013}, but this can lead to difficulties in coupling radiation into the cavity and in drilling ports so as to not destroy the Q.

A far better solution is to use a Fabry-Perot resonator, the particular type we use being either a semi-confocal or a confocal resonator. Strictly, the confocal resonator consists of two equivalent concave mirrors arranged coaxially such that the separation between them (d) is equal to their radius of curvature (R). In practice the system will still resonate if the separation is altered or if the mirrors have different radii of curvature and we shall still refer to this as a confocal system. The semi-confocal resonator consists of a plane and a concave mirror arranged such that the principal axis of the concave mirror is perpendicular to the plane mirror surface. If the separation of these mirrors is d then this system can be regarded as equivalent to placing a plane mirror at the midpoint of two identical concave mirrors of separation 2d. The semi-confocal system therefore differs from the 'confocal' system only in that every other resonant mode is missing. This is a point more readily appreciated once the nature of the cavity modes has been discussed.

The general theory of Fabry-Perot resonators and their modes has been reviewed by Kogelnik and Li (4) and by Yariv (5). Only information relevant to confocal (and semi-confocal) resonators will be presented here.

First, it will be necessary to discuss the propogation of electromagnetic beams. Starting from Maxwell's equations an electromagnetic wave equation can be derived, from which the electric and magnetic field vectors, $\underline{E}$ and $\underline{H}$ respectively, in a homogeneous charge-free medium can be shown to take the general form

$$\begin{aligned} \underline{E} &= \underline{E}_0 \exp(i\omega t - i\underline{k}.\underline{r} + i\phi) \\ \underline{H} &= \underline{H}_0 \exp(i\omega t - i\underline{k}.\underline{r} + i\phi) \end{aligned} \qquad (4.1)$$

where $\underline{E}_0$ and $\underline{H}_0$ are the amplitudes of the wave vectors, $\underline{k}$ is the propogation vector along the direction vector $\underline{r}$, ω is the frequency of the radiation and ϕ is a phase factor. $\underline{E}$, $\underline{H}$ and $\underline{k}$ can be shown to be mutually orthogonal. We shall assume the wave is propogated in the z direction only, and so $\underline{k}.\underline{r}$ is replaced by kz. The wavefunctions (4.1) lead to planar wavefronts and uniform intensity distributions perpendicular to z whereas curved wavefronts and non-uniform transverse intensity distributions are more realistic. These requirements can be taken into account by replacing the amplitude constant $\underline{E}_0$ by a new function ψ containing exponentials with complex arguments:

$$\underline{E} = \psi \exp(-ikz + i\omega t) \qquad (4.2)$$

and similarly for $\underline{H}$.

One solution for ψ is of the form

$$\psi = \exp\left[-iP(z) - \frac{ik(x^2 + y^2)}{2q(z)}\right] \qquad (4.3)$$

where P(z) and q(z) are complex parameters describing the propogation of the beam. P(z) is a complex phase shift and q(z) a complex radius of curvature giving the required curved wavefronts and the non-uniform intensity distribution.

It is far more convenient to introduce two real beam parameters R(z) and ω(z), which are defined as follows:

$$\frac{1}{q(z)} = \frac{1}{R(z)} - \frac{i\lambda}{\pi\omega^2(z)} \qquad (4.4)$$

with the complex beam parameter at the origin of the z axis being given by

$$q(z = 0) = q_0 = \frac{i\pi\omega_0^2}{\lambda} \qquad (4.5)$$

The physical interpretation of these two parameters is as follows: ω(z) is a measure of the non-uniform intensity distribution and is known as the spot size. ω is defined as the distance measured normal to the axis of propogation at which the intensity is $\frac{1}{e}$ of that on axis. ω_0 is the minimum spot size, or beam waist, and since from (4.5) $\omega = \omega_0$ at z = 0 we see that the choice of origin for the z axis is at the beam waist. R(z) is the real radius of curvature of the wavefronts at a distance z from the origin. Using the above definition of the origin, R(z) and ω(z) can be obtained:

$$R(z) = z\left[1 + \left(\frac{\pi \omega_0^2}{\lambda z}\right)^2\right] \tag{4.6}$$

$$\omega(z) = \omega_0^2\left[1 + \left(\frac{\lambda z}{\pi \omega_0^2}\right)^2\right] \tag{4.7}$$

It follows from substitution of $z = 0$ into (4.6) that the wavefronts at the beam waist are planar.

The solution (4.2) of the electromagnetic wave equation can be rewritten

$$\underline{E} = \frac{\omega_0}{\omega(z)} \exp\left(\frac{-r^2}{\omega(z)^2}\right) \exp\left(\frac{-ir^2k}{2R(z)}\right) \exp\left(-ikz + i\phi\right) \exp\left(i\omega t\right) \tag{4.8}$$

where $\phi = \arctan\left(\dfrac{\lambda z}{\pi \omega_0^2}\right)$

and $r^2 = x^2 + y^2$

The first exponential in (4.8) represents the non-uniform intensity distribution, the second and third describe the beam divergence. Figure 2 illustrates the profile of this beam. As can be seen, the intensity profile is Gaussian in shape and hence these beams are commonly referred to as Gaussian beams. This particular beam shape is the fundamental mode.

Higher order modes also exist and these have the form

$$\underline{E} = \frac{\omega_0}{\omega} \exp\left(\frac{-r^2}{\omega^2}\right) \exp\left(\frac{-ir^2k}{2R(z)}\right) \exp\left(-ikz + i\phi\right) \exp\left(i\omega t\right)$$

$$\times \left(\frac{\sqrt{2}\, r}{\omega}\right)^l L_p^l\left(\frac{2r^2}{\omega^2}\right) \tag{4.9}$$

where $\phi = (2p + l + 1) \arctan\left(\dfrac{\lambda z}{\pi \omega_0^2}\right)$

L_p^l is a Laguerre polynomial with radial and angular mode numbers p and l respectively. Since $L_0^l = 1$ it follows that (4.8) is a special case of (4.9), with $p = l = 0$. Since the electric and magnetic field vectors are both orientated perpendicular to the z axis these modes can be described as TEM_{pl} modes.

We are now in a position to describe confocal resonator systems. The elec-

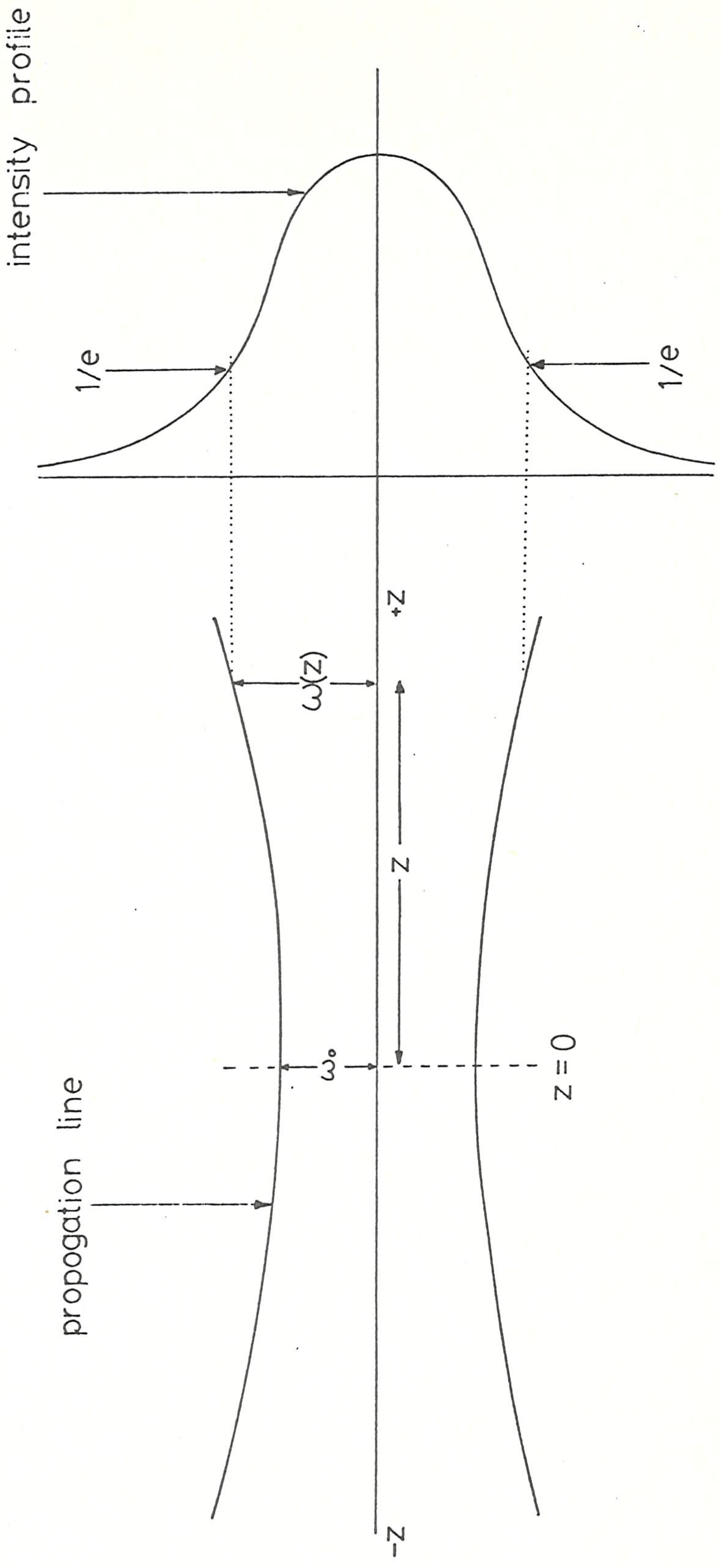


Figure 2 Propogation lines and intensity profile of a Gaussian Beam.

tromagnetic radiation within the cavity is adequately described by a function of the form of (4.9), i.e. by a Gaussian beam. Under certain conditions a standing wave can result from the reflections from the two mirrors. It is apparent that, in order to get reflections, the radii of curvature of the mirrors must be equal to those of the wavefronts at that point along the principal (z) axis. Figure 3 illustrates a typical two-concave-mirror system. The coupling iris through which radiation enters the cavity is not indicated. It could be in the centre of either mirror.

The condition for resonance is that the phase shift between the mirrors is π, or a multiple thereof. Consider the simpler case where $R_1 = R_2 = R$. The phase shift from A to B must take the general form

$$(kz - \phi) = q\pi \qquad (4.10)$$

where q is an integer.

It is now possible to derive the beam waist and resonant frequencies for this system. Since $R(z) = R$ at $z = d/2$ then from (4.6) and (4.7) we obtain

$$\omega_0^2 = \frac{\lambda}{2\pi}\sqrt{(2R - d)\,d} \qquad (4.11)$$

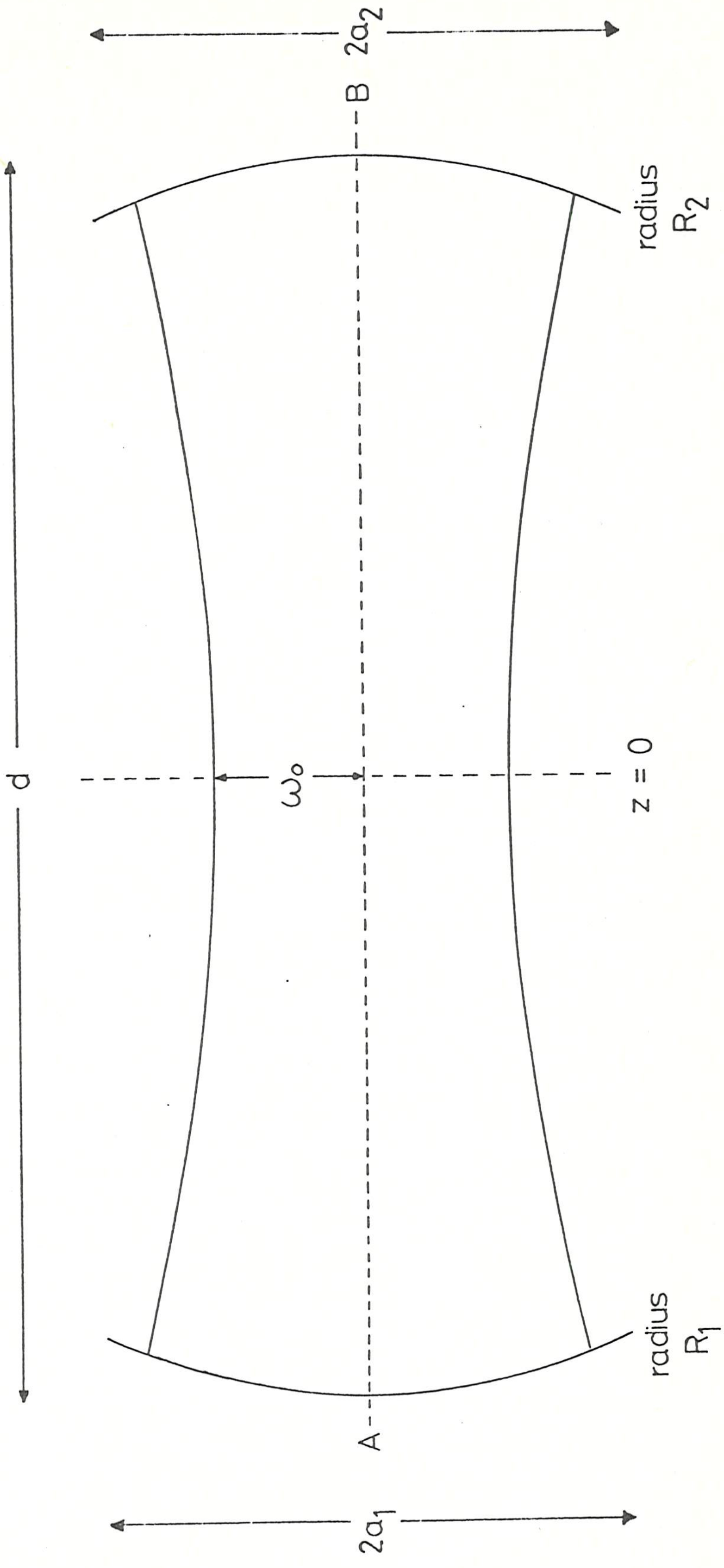
which on substitution into (4.10) leads to

$$\nu = \frac{c}{2d}\left[q + \frac{1}{\pi}(2p + 1 + 1)\arccos\left(1 - \frac{d}{R}\right)\right] \qquad (4.12)$$

q is known as the longitudinal mode number, and the cavity modes can be designated TEM_{plq}. For given values of p and l, and for fixed d and R, there is a succession of resonances the separation between consecutive resonances being $\frac{c}{2d}$, known as the free spectral range, $\Delta\nu$.

The strong dependence of ν on d can be used to our advantage. It is possible to show by differentiation of (4.12) with respect to d that a change of $\Delta\nu$ in the resonant frequency ν can be brought about by altering the length d by approximately half a wavelength. This leads to the possibility of constructing a tunable cavity, since quite modest changes in d (say $\pm\frac{1}{2}$cm) can produce large changes in the resonant frequencies (say $\pm$2GHz). A change of $\Delta\nu$ in all of the resonant modes is all that is required for the cavity to be continuously tunable over a very wide frequency range, a possibility which does not exist for the reflection cavities discussed previously.

Figure 3 A Fabry-Perot resonator constructed from two concave mirrors.



Expressions corresponding to (4.11) and (4.12) for the case where $R_1 \neq R_2$ are more complicated and so will not be quoted here. They have been given by Kogelnik and Li (4).

As has been mentioned already, the wavefronts at the beam waist are planar. Hence a plane mirror could be placed at the beam waist to form a new resonant system, but with essentially the same characteristics as the two-concave-mirror one. This is the semi-confocal resonator. The only difference is that, since the phase shift between mirrors has to be a multiple of π, only those frequencies obtained from use of the confocal formulae (with d as twice the semi-confocal separation) with even q values will be supported, i.e. every other mode will be absent. The apparent free spectral range for a semi-confocal system is twice that of the corresponding confocal system.

In designing a Fabry-Perot resonator for e.p.r. purposes there are various points to bear in mind. First, in order to pass radicals through the mirror gap it is necessary to enclose the mirrors and incorporate this space into the vacuum line. This is easily achieved by using a glass or perspex cylinder into the ends of which the mirrors will fit (with suitable vacuum seals). The glass cylinder is perhaps the more convenient as then standard glass joints can be used throughout the vacuum line. Since only the mirrors are responsible for supporting the modes the inlet and outlet ports built into this cylinder can be any convenient size - there are no problems arising from loss of power through the ports as there are for the reflection cavities. In addition it is not too difficult to transmit 100kHz modulation through the cylinder walls. Microwave cavities are constructed from highly conductive metals which have small skin depths, δ. For instance, for copper the skin depth at 100kHz is 0.2mm and so the current density has dropped to $\frac{1}{e}$ of its original value at this depth of penetration. To combat this attenuation either very large modulation power levels must be used, or the cavity walls through which the modulation is to pass must be a very thin layer of conducting metal (preferably deposited onto some non-conducting material so as to retain mechanical strength). Since glass and perspex are poor conductors their skin depths are extremely large, of the order of 10^3m for 100kHz frequencies, and so the modulation will penetrate the cell walls of a Fabry-Perot resonator easily.

Secondly, from the point of view of sensitivity, the maximum on-axis intensity of radiation is required, which means that the TEM_{00q} modes should be used. To prevent too much power being diverted into higher order modes these other modes have to be discriminated against. Higher order modes have their maximum intensity on-axis, but unlike the TEM_{00q} modes they also have a non-zero intensity at a certain distance off-axis. If these satellite regions can be discriminated against then the dominant modes will be the TEM_{00q}. This can be arranged by using mirrors of such a width (a) that these satellites fall outside the mirrors and hence are not reflected. Losses from around the sides of the mirrors in this way are known as diffraction losses. Other losses also occur in the system, such as from absorption by the dielectric medium, scattering off imperfections in the mirrors, poor coupling of radiation into or out from the cavity and so on.

Thirdly, a resonant system is not necessarily a stable one. If we define

$$g_1 = 1 - \frac{d}{R_1}$$

$$g_2 = 1 - \frac{d}{R_2}$$

then the system is stable only if

$$0 < g_1 g_2 < 1 \qquad (4.13)$$

Finally, we have to determine the Fresnel number N, defined by

$$N = \frac{a_1 a_2}{\lambda d} \qquad (4.14)$$

An estimate of diffraction losses for the TEM_{00q} modes can be obtained for given values of g_1, g_2 and N, and it turns out that for fixed g_1 and g_2 these losses are least when N is greatest. The Fresnel number can be related to the phenomenon of Newton's rings and so the higher the value of N, the more radial modes there are and the more likely higher modes are to be supported. To discriminate against such modes a system with an N value close to 1 must be used. Taken in conjunction with earlier statements, the optimum N values for our purposes are between 1 and 2, preferably nearer 2. The values of a_1, a_2, R_1, R_2 and d have therefore to be carefully chosen. Nevertheless, it is possible to obtain high Q-factors for these cavities, typically ~6000 for ~26GHz and increasing rapidly for higher frequencies.

It should be apparent that the Fabry-Perot resonator offers several advantages over the reflection cavities - they allow e.p.r. experiments to be performed at higher frequencies than for the reflection type; it is possible to observe all types of magnetic and electric dipole transitions simply by altering the orientation of the waveguide coupling into the cavity; they can be tuned easily over a large frequency range; there is no problem in the sizes of gas ports; and finally, there is no problem in getting a modulation signal through the cell walls.

References to Chapter 4

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CHAPTER 5

A DETERMINATION OF g-FACTORS FOR THE ^{16}OH RADICAL

5.1 Introduction

The OH radical probably qualifies as being the most extensively studied free radical. Since its detection early in this century, it has been subjected to many theoretical and experimental studies. We are only interested in the rotational energy levels of the ^{16}OH molecule and the studies pertaining to these.

There are several reasons for the great interest taken in the OH molecule. First, the rotational energy levels are complicated by various uncoupling effects, which arise from the fast rotation of the molecule, since it is so light. There are thus some rather interesting features in the rotational spectrum which can give information on the electronic structure (1). The description of these interactions poses a problem for the experimentalist, who needs to determine a suitable effective Hamiltonian before he can analyse his data. As far as the theoretician is concerned, these uncoupling effects provide a severe test of ab initio calculations of molecular parameters.

Secondly, OH is a molecule of great astronomical significance. Radio-astronomers have detected its presence (2) in numerous interstellar gas clouds and in comet tails. Because of its great abundance in interstellar space it is particularly useful for estimations of relative velocities of sources, though an accurate determination in the laboratory of the molecular constants in a necessary precursor of such work. A further interesting example of the way in which interstellar OH signals have been used is in the estimation of the minute magnetic fields present in collapsing gas clouds (3), using a comparison of left and right circularly polarised spectra. It is likely that OH plays an important role in interstellar chemistry, such reactions subsequently leading to the formation of larger molecules. The OH radical is therefore a potentially useful probe molecule for the study of the physical and chemical development of interstellar gas clouds.

Finally, OH is very easily made in the laboratory and has a relatively long lifetime, around $\frac{1}{3}$ sec., so that sufficient concentrations can be generated to allow easy detection. Indeed, this molecule is often detected during the search for new radicals, sometimes even from the most unlikely combinations of reactants. The reason for the long lifetime of OH is that, under favourable conditions, a particular regenerative process occurs.

All this notwithstanding, there are still aspects that have not been extensively investigated, a case in point being the molecular g-factors. Radford (4, 5), in the first gas phase e.p.r. experiments on unstable molecular radicals, has investigated the microwave Zeeman effect and has determined the effective g-values. These effective g-values are determined phenomenologically - each describes the overall rate of tuning with applied magnetic field of a single rotational level. Of far more value are the fundamental molecular g-factors, which relate to the different interactions of molecular angular momenta with the external magnetic field, since these give direct information on the electronic structure of the molecule. The effective g-factors found by Radford can be written as linear combinations of the molecular g-factors. To our knowledge, no analysis has yet been performed to determine the molecular g-factors and so to remedy this omission we have performed an analysis of the e.p.r. spectra of seven rotational levels of the ground vibronic state of the ^{16}OH radical. Radford's data for five of these levels are used, transition frequencies for the other two levels being measured at the University of Southampton.

These g-factor determinations are not likely to be of great value to radioastronomers as far as estimations of magnetic fields in gas clouds are concerned. The phenomenological g-factors are quite suitable for this purpose. However, the advantage of the molecular g-factors is that since they are related to more fundamental molecular quantities, such as electron distributions, they are capable of giving far more information on the electronic structure than are the effective g-factors.

In the following section a brief outline of the theory of the rotational energy levels is given, while in section 3 the previous studies are described. Section 4 deals with the experiments performed in this laboratory on the $^2\Pi_{3/2}$ J = 9/2 levels and in sections 5 to 7 we present the form of the effective Hamiltonian used in our analysis and compare this with previous Hamiltonians. In the final two sections the results of this analysis are presented and discussed.

5.2 Rotational Levels of a Diatomic Molecule in a $^2\Pi$ Electronic State

In this section we describe the rotational energy levels for a molecule in a $^2\Pi$ state, with particular reference to the OH molecule. Initially we look at the energy levels in the absence of rotation of the nuclei and then the effects on these fine structure states on introduction of the rotational and associated uncoupling interactions are considered. The effects of nuclear spins will be ignored for the time being.

We must first decide on a suitable set of basis functions. Since for most molecules in $^2\Pi$ states the spin-orbit coupling is large, so that both $\underline{L}$ and $\underline{S}$ are coupled strongly to the internuclear axis and the quantum numbers Λ and Σ are well-defined, then wavefunctions conforming to a Hund's case a) coupling scheme are most appropriate. Case a) wavefunctions are of the form

$$|\eta\Lambda;\ S\Sigma;\ J\Omega M\rangle$$

where the quantum numbers that define this function have the significance described in chapter 2. For a $^2\Pi$ electronic state these quantum numbers have certain allowed values, which are as follows:

$$\begin{aligned} \Lambda &= \pm 1 \\ S &= 1/2 \\ \Sigma &= \pm 1/2 \\ J &= 1/2,\ 3/2,\ \ldots \end{aligned} \tag{5.1}$$

From the linear molecule restriction, the values Ω is allowed to take are

$$\Omega = \Lambda + \Sigma = \pm 1/2,\ \pm 3/2 \tag{5.2}$$

subject to the restriction $J \geqslant |\Omega|$.

In the absence of rotation, states with the same value of $|\Omega|$ are degenerate and so there are two fine structure states, labelled $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ according to the value of $|\Omega|$. The wavefunctions corresponding to these states are of the form

$$\begin{aligned} |^2\Pi_{1/2}\rangle &= |\Lambda = \pm 1;\ \Sigma = \mp 1/2\ \rangle \\ |^2\Pi_{3/2}\rangle &= |\Lambda = \pm 1;\ \Sigma = \pm 1/2\ \rangle \end{aligned} \tag{5.3}$$

and the separation in energies of these states is a measure of the spin-orbit coupling constant, A. Obviously if the spin-orbit coupling is large then these two fine structure states will be well separated. These states can further be classified as regular or inverted according to whether the quantity (A - 2B) is positive or negative respectively. This quantity governs the size of the splitting of the fine structure states and hence for a regular state the $^2\Pi_{1/2}$ state is lower in energy than for the $^2\Pi_{3/2}$

state, whereas for an inverted state the reverse applies.

So far we have considered the fine structure states for a good case a) molecule, but the OH radical is not well described by case a) wavefunctions. There are two reasons for this, not entirely independent. First, because the molecule rotates rapidly, $\underline{S}$ is extensively uncoupled from the internuclear axis, and the quantum number Σ is no longer well-defined. The quantum number Ω therefore begins to lose significance as the uncoupling gets larger and so it is no longer valid to refer to the fine structure states as $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$. This is because the spin-uncoupling, as it is known, has caused these two states to be extensively mixed and so they lose their separate identities. The labels $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ strictly only apply to a pure case a) $^2\Pi$ state. In addition, the spin-orbit coupling constant for OH is relatively small, since it is so light, and hence the fine structure states are quite close together (approximately 140cm^{-1} apart). The proximity of the fine structure states in OH serves to enhance the mixing of these states. In the extreme case of complete uncoupling of $\underline{S}$ from the internuclear axis, in which case Σ and Ω have no significance whatsoever, we have a Hund's case b) coupling scheme. The labels $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ are then no longer valid and so wavefunctions must be chosen which conform to a case b) scheme. The coupling scheme for OH is intermediate between cases a) and b), so the labels $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ do not strictly apply. It is convenient however to retain the case a) formalism to deal with the OH rotational levels.

Although uncoupling effects have briefly been considered above, their origin has not been indicated on any mathematical grounds. These uncoupling interactions arise on introduction into the Hamiltonian of terms describing the rotational motion of the nuclei. The Hamiltonian for the spin-orbit and rotational interactions is as follows:

$$H = AT^1(\underline{L}).\ T^1(\underline{S}) + BT^1(\underline{J}-\underline{L}-\underline{S}).\ T^1(\underline{J}-\underline{L}-\underline{S}) \qquad (5.4)$$

where a greatly simplified form of the microscopic spin-orbit Hamiltonian is used, known as the phenomenological spin-orbit Hamiltonian. The microscopic spin-orbit Hamiltonian allows more electronic states to be mixed into the ground state than does the phenomenological form. This is because the latter is based on Van Vleck's pure precession hypothesis, in which $\underline{L}^2$ is assumed to be a constant of the motion, i.e. L is a well defined quantum number.

The Hamiltonian (5.4) can be expanded in a molecule-fixed axis system to obtain the following:

$$\begin{aligned} H \;=\; & A\sum_{q}(-1)^{q}\,T^{1}_{q}(\underline{L})\,T^{1}_{-q}(\underline{S}) + B\sum_{q}(-1)^{q}\Big\{T^{1}_{q}(\underline{J})\,T^{1}_{-q}(\underline{J}) \\ & + T^{1}_{q}(\underline{L})\,T^{1}_{-q}(\underline{L}) + T^{1}_{q}(\underline{S})\,T^{1}_{-q}(\underline{S}) + 2T^{1}_{q}(\underline{L})\,T^{1}_{-q}(\underline{S}) \\ & - 2T^{1}_{q}(\underline{J})\,T^{1}_{-q}(\underline{S}) - 2T^{1}_{q}(\underline{J})\,T^{1}_{-q}(\underline{L})\Big\} \end{aligned} \qquad (5.5)$$

where $q = 0, \pm 1$.

Since the $q = 0$ component is defined to be equivalent to the component along the internuclear (z) axis then we have the relations

$$T^{1}_{0}(\underline{L}) \equiv L_{z} = \Lambda$$

$$T^{1}_{0}(\underline{S}) \equiv S_{z} = \Sigma$$

$$T^{1}_{0}(\underline{J}) \equiv J_{z} = \Omega$$

which on substitution into (5.5) leads to

$$\begin{aligned} H \;=\; & A\Lambda\Sigma \\ & + B\left[J(J+1) + S(S+1) - 2\Omega\Sigma - \Lambda^{2}\right] \\ & + B\sum^{\dagger}_{q=\pm1}(-1)^{q}\,T^{1}_{q}(\underline{L})\,T^{1}_{-q}(\underline{L}) \\ & - 2B\sum^{\dagger}_{q=\pm1}(-1)^{q}\,T^{1}_{q}(\underline{J})\,T^{1}_{-q}(\underline{S}) \\ & + (2B + A)\sum^{\dagger}_{q=\pm1}(-1)^{q}\,T^{1}_{q}(\underline{L})\,T^{1}_{-q}(\underline{S}) \\ & - 2B\sum^{\dagger}_{q=\pm1}(-1)^{q}\,T^{1}_{q}(\underline{J})\,T^{1}_{-q}(\underline{L}) \end{aligned} \qquad (5.6)$$

The first term in (5.6) is responsible for the splitting between the fine structure states and it is readily seen by substitution of $\Lambda = \pm 1$ and $\Sigma = \pm 1/2$, the relevant quantum numbers for a $^{2}\Pi$ state, that two such states are obtained, differing only in the value of $|\Omega| = |\Lambda + \Sigma|$, and separated by an energy equal to A, as noted previously. The second term, arising from the diagonal part of the rotational Hamiltonian, lifts the degeneracy of the fine structure states, giving rise to a sub-manifold of rotational levels for each of the fine structure states. The third term, $B \sum_q^{\dagger} (-1)^q \, T_q^1 (\underline{L}) \, T_{-q}^1 (\underline{L})$, equivalent to $B(L_x^2 + L_y^2)$ in the Cartesian notation, adds a constant term to all of the rotational levels, although higher order perturbation terms involving this term will not necessarily impart a constant shift to all the energy levels. To first order we are justified in ignoring this term as we are only concerned with the relative energies of the rotational levels.

The fourth term, $- 2B \sum_q^{\dagger} (-1)^q \, T_q^1 (\underline{J}) \, T_{-q}^1 (\underline{S})$, is the familiar spin-uncoupling term given in equation (3.7) of chapter 3. Its effect has already been discussed earlier in this section, namely, this term accounts for the uncoupling of the electron spin from the internuclear axis as the molecule rotates. Non-zero matrix elements of this operator occur between states of different Σ value but the same Λ value, i.e. between states of different $|\Omega|$. This term is hence responsible for mixing the two fine structure states together, and so for the deviations towards case b) behaviour. The smaller the separation between the fine structure states then the more extensively they will be mixed. Similarly, the faster the molecule rotates then the more the spin is uncoupled from the axis. A useful indication of the magnitude of the spin-uncoupling is given by $Y = A/B$, the ratio of the spin-orbit coupling and rotational constants: the smaller the value of Y then the larger the spin-uncoupling. Since for OH the spin-orbit coupling constant is small and the rotational constant quite large then Y is quite small, thus giving some quantitative description of the marked deviation towards case b) behaviour. The experimental value of Y for OH is approximately -7.5, where Y is negative because A is negative. Simple arithmetic shows that $(A - 2B)$ is a negative quantity and so OH is an inverted state, in which for a given J the $^2\Pi_{3/2}$ levels are lower in energy than those of the $^2\Pi_{1/2}$ state.

The final two terms in (5.6) are, respectively, the off-diagonal contributions denoting the uncoupling of $\underline{S}$ from $\underline{L}$ and the L-uncoupling terms given in equation (3.6) of chapter 3, the latter representing the uncoupling of $\underline{L}$ from the internuclear axis. Each of these terms have non-zero matrix elements between states differing in the value of Λ by 1 and hence are responsible for the admixture of excited electronic states into the $^2\Pi$ ground state. The effect of these interactions is to give different shifts to the states with different Λ. This lifting of the Λ-degeneracy of the rotational levels is known as Λ-doubling. The states that are mixed directly into a $^2\Pi$ state by these two interactions can only be Σ or Δ states, and it will subsequently be shown that to a high degree of approximation the Λ-doubling arises predominantly from the admixture of Σ states only.

Now in the absence of an electric field the total Hamiltonian commutes with the space-fixed inversion (parity) operator E*, or, in other words, they possess a common set of eigenfunctions $|\psi\rangle$:

$$\begin{aligned} H|\psi\rangle &= E|\psi\rangle \\ E^*|\psi\rangle &= \pm|\psi\rangle \end{aligned} \qquad (5.7)$$

where E represents the energy and + or - the relative parity of the eigenfunction. The eigenfunctions $|\psi\rangle$ in this case possess well-defined parity. If these wavefunctions are used as basis functions then there will be no matrix elements of the total Hamiltonian connecting states of opposite parity.

Consider the manner in which the case a) basis functions that we have adopted so far transform under the parity operator. As mentioned in chapter 3, this requires a consideration of how the Euler angles transform under E*

$$E^*\,|\eta\Lambda;\, S\Sigma;\, J\Omega M\rangle = (-1)^{J-S}\;|\eta -\Lambda\,;\, S -\Sigma\,;\, J -\Omega\; M\rangle \qquad (5.8)$$

This is analogous to the expression given in equation (3.23) of chapter 3, the $\pm$ in the latter expression referring to Σ states only. It follows from (5.8) that these basis functions do not possess well-defined parity. We therefore define a parity basis set by taking the linear combinations

$$\begin{aligned} |\eta\Lambda;\, S\Sigma;\, J\Omega M;\, \pm\rangle &= |\pm\rangle \\ &= \frac{1}{\sqrt{2}}\left\{|\eta\Lambda;\, S\Sigma;\, J\Omega M\rangle \pm (-1)^{J-\frac{1}{2}}\,|\eta -\Lambda\,;\, S -\Sigma\,;\, J -\Omega\; M\rangle\right\} \end{aligned} \qquad (5.9)$$

This transforms under the parity operator as follows:

$$\begin{aligned} E^*|\pm\rangle &= \frac{1}{\sqrt{2}}\left\{(-1)^{J-\frac{1}{2}}\;|\eta -\Lambda\,;\, S -\Sigma\,;\, J -\Omega\; M\rangle \pm |\eta\Lambda;\, S\Sigma;\, J\Omega M\rangle\right\} \\ &= \pm|\pm\rangle \end{aligned} \qquad (5.10)$$

and hence these new wavefunctions have well-defined parity.

In the case of the non-parity wavefunctions the eigenvalues for a given J are obtained by diagonalisation of a 4 x 4 secular determinant, involving the four basis functions

$$\left| {}^2\Pi_{3/2} \;\; \Lambda = +1 \right\rangle \; ; \; \left| {}^2\Pi_{3/2} \; \Lambda = -1 \right\rangle$$
$$\left| {}^2\Pi_{1/2} \;\; \Lambda = +1 \right\rangle \; ; \; \left| {}^2\Pi_{1/2} \; \Lambda = -1 \right\rangle \qquad (5.11)$$

For the parity wavefunctions there are still four basis functions, labelled

$$\left| {}^2\Pi_{3/2}; + \right\rangle \qquad \left| {}^2\Pi_{3/2}; - \right\rangle$$
$$\left| {}^2\Pi_{1/2}; + \right\rangle \qquad \left| {}^2\Pi_{1/2}; - \right\rangle \qquad (5.12)$$

but since there are no matrix elements between states of opposite parity then the 4 x 4 secular determinant factorises into two 2 x 2 determinants. The advantage in constructing a secular matrix from parity basis functions is therefore that we gain considerably in the ease of computation of the eigenvalues.

Matrix elements of the Hamiltonian in the parity basis are related to those in the non-parity basis as follows:

$$\left\langle {}^2\Pi\, J; \pm \right| H \left| {}^2\Pi\, J'; \pm \right\rangle = \left\langle J; \; \Lambda = \pm 1 \right| H \left| J'; \; \Lambda = \pm 1 \right\rangle$$
$$\pm (-1)^{J'-\frac{1}{2}} \left\langle J; \; \Lambda = \pm 1 \right| H \left| J'; \; \Lambda = \mp 1 \right\rangle \qquad (5.13)$$

It is apparent from (5.13), or from (5.12), that, for levels of a given J, the energies of levels of opposite parity differ by a Λ-doubling interval. Hence the two levels of a Λ-doublet have opposite parity, and can be labelled + or - accordingly. The phase factor $(-1)^{J-\frac{1}{2}}$ in (5.13) means that the relative parities of upper and lower Λ-doublets alternates for successive J levels.

In order to describe the rotational energy levels of a $^2\Pi$ state in terms of $^2\Pi$ basis functions only, a suitable effective Hamiltonian is required, and so, to account for the Λ-doubling phenomenon, terms must be included in the effective Hamiltonian that, in first order, mimic the higher order effects of the final two terms in (5.6). The derivation of such a Hamiltonian will be postponed for the time being.

Figure 1 shows the general disposition of the rotational energy levels for an inverted $^2\Pi$ electronic state, the levels connected by braces being the Λ-doublets.

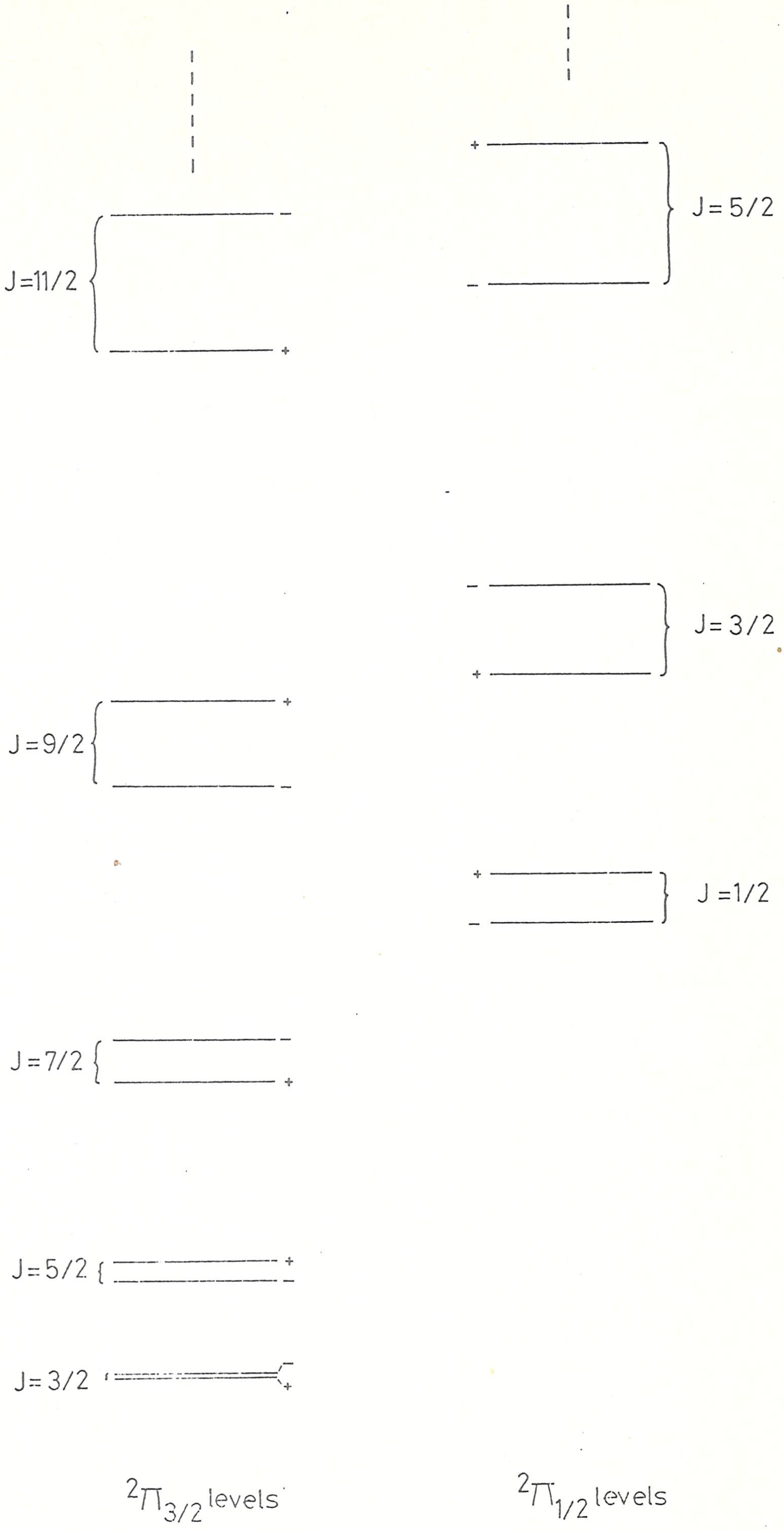


Figure 1 Schematic representation of rotational energy levels for an inverted $^2\Pi$ electronic state.

We merely note at this stage that since the hydrogen atom has a nuclear spin of $I = \frac{1}{2}$ then hyperfine effects must also be considered. Each of the rotational levels in figure 1 are thus further split into doublets, corresponding to the two allowed orientations of the nuclear spin. If the coupling scheme

$$\underline{F} = \underline{J} + \underline{I}$$

is used then these hyperfine levels can be labelled by the quantum number F, given by

$$F = J - \tfrac{1}{2} \quad \text{or} \quad J + \tfrac{1}{2}$$

There is a further degeneracy associated with each of the rotational levels and this arises from the quantisation of the total angular momentum, $\underline{J}$ (or $\underline{F}$ if nuclear spin is included), in the space-fixed axis system. Consider the case where nuclear spin is not included. As described in chapter 2, the quantum number m_J relates to the projection of J along the space-fixed z axis, and takes the 2J + 1 values

$$m_J = J, J - 1 \ldots -J.$$

In the absence of external magnetic or electric fields the (2J + 1) states $|J\, m_J\rangle$ are degenerate. On application of a magnetic field, however, the degeneracy of these levels is lifted, this being the well-known Zeeman effect. The Zeeman energies are given by a relation of the form

$$E_{Zeeman} = -m_z B_0 \tag{5.14}$$

where B_0 is the magnetic flux density and m_z the component of the magnetic moment of the molecule along the field direction. The latter is related to the m_J value by the expression

$$m_z = -g_J \mu_B \, m_J \tag{5.15}$$

where μ_B is the Bohr magneton and g_J the effective rotational g-factor. This effective g-factor is compounded from more fundamental molecular g-factors, the dominant contributions arising from the electron spin and orbital motions. The values of these particular g-factors are very close to the well known free electron values

$$\begin{aligned} g_S &= 2.00232 \\ g_L &= 1.000 \end{aligned} \tag{5.16}$$

For a pure case a) coupling scheme the effective g-factor is proportional to the quantity ($g_S\Sigma + g_L\Lambda$) and it is immediately apparent therefore that the effective g-factor for a $^2\Pi_{1/2}$ state, in which the electron orbital and spin magnetic moments effectively oppose one another, is approximately zero. Since the magnetic moment is so small then the Zeeman splitting of the $^2\Pi_{1/2}$ rotational levels is almost negligible.

Now, as mentioned in chapter 4, the principle of electron paramagnetic resonance (e.p.r.) spectroscopy is that the sample is irradiated by electromagnetic radiation of a fixed frequency and the Zeeman effect is utilised to tune the energy separations between various pairs of levels into resonance with this fixed frequency. If the g-factor is very small then either it will not be possible to tune the relevant levels into resonance at all or, even if the levels can be tuned, since the levels tune so slowly the absorption line will be so broad as to be undetectable. It is not likely to be possible to observe an e.p.r. spectrum arising from a pure $^2\Pi_{1/2}$ state.

Consider, however, the situation for a pure case b) coupling scheme. The electron spin angular momentum is completely decoupled from the internuclear axis and so the state labels $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ have no significance. The magnetic moments arising from the electron spin and orbital angular momenta do not therefore lie along the same axis and so the effective g-factor is non-zero for all the rotational levels.

The coupling scheme for OH is intermediate between cases a) and b), but we have retained the case a) formalism for convenience. In this case, the effective g-factors for the $^2\Pi_{1/2}$ levels are non-zero, although quite small. This situation can be regarded as an acquisition of case b) behaviour by the case a) wavefunctions as the coupling scheme deviates towards case b), or, in other words, as the spin uncoupling becomes larger so the fine structure states become more extensively mixed and more $^2\Pi_{3/2}$ character is introduced into the $^2\Pi_{1/2}$ states. The magnetic moment of the $^2\Pi_{1/2}$ states is therefore "borrowed" from the $^2\Pi_{3/2}$ states and so it is possible to observe e.p.r. spectra arising from the $^2\Pi_{1/2}$ state of OH, although the lines are much weaker and much broader than in spectra from $^2\Pi_{3/2}$ levels. The weakness of the $^2\Pi_{1/2}$ lines is a result of the smaller Boltzmann population rather than being due to the smaller g-factors. We note that since the $J = \frac{1}{2}$ levels exist only for the $^2\Pi_{1/2}$ state then there can be no mixing with the $^2\Pi_{3/2}$ state and so the g-factor for these levels should be essentially zero, even for a light molecule such as OH.

5.3 Previous Studies of the ^{16}OH Radical

As has already been mentioned, the OH radical has been the subject of a great many studies, covering a wide range of techniques. We are only interested in those studies giving information on the rotational energy levels.

Dieke and Crosswhite (6) have performed an extensive analysis of the vacuum ultra-violet spectrum of OH, the radical being produced in an oxy-acetylene flame. Values for the rotational constant B, centrifugal distortion parameter D_B and the fine-structure parameter Y (= A/B) were obtained from this work, which were more accurate than from previous studies. However, the linewidths inherent in this type of experiment are quite broad (typically $\sim 0.1 - 0.5\text{cm}^{-1}$) and so the effects of some of the smaller interactions cannot be resolved. High resolution techniques, such as studies in the microwave region or molecular beam methods, must therefore be adopted if these smaller effects are to be detected.

Since the OH molecule is so light, the spacings between successive rotational levels are quite large - about 100cm^{-1} for the lower levels. The rotational spectrum of OH, arising from transitions between these levels, therefore lies in the far infra-red, where the resolution is still quite low (typically $\sim 10^{-3}\text{cm}^{-1}$). Fortunately there are transitions in this molecule that occur at microwave frequencies and so measurements of high precision can be made. The observed microwave spectrum in fact arises from transitions between the Λ-doublets from a given rotational level. These Λ-doubling transitions are therefore electric-dipole allowed since they ~~cannot~~ connect states of opposite parity.

The first zerofield microwave absorption studies of Λ-doubling in OH were performed by Dousmanis, Sanders and Townes (7), in this case the radical being detected in the products of a microwave discharge in water vapour

$$H_2O \longrightarrow OH + \text{other products} \qquad (5.17)$$

The observed transitions arose from the J = 3/2 and 5/2 levels of the $^2\Pi_{1/2}$ state, and from the J = 7/2, 9/2 and 11/2 levels of the $^2\Pi_{3/2}$ state, the frequencies lying in the range 7700 to 37000MHz. The accuracies of these measurements were, at best, within 50kHz, which was sufficient to gain information on the phenomenon of Λ-doubling and to give estimates of the magnetic hyperfine parameters. This list of zero-field measurements has subsequently been extended by Poynter and Beaudet (8), Radford (9) and Ball and coworkers (10, 11), who were also able to improve on the accuracy of the lines measured by Dousmanis et al (7).

The most accurate determinations of zero-field Λ-doubling frequencies come from molecular beam studies. Measurements of the $^2\Pi_{3/2}$ J = 3/2 lines were obtained by ter Meulen and Dymanus (12) using a beam maser spectrometer, these frequencies being accurate to within 100Hz. The $\Delta F = 0$ transitions from the $^2\Pi_{3/2}$ J = 9/2 levels were remeasured by ter Meulen (13) using the same technique. A molecular beam electric resonance (MBER) experiment was performed by Meerts and Dymanus (14) to remeasure the $^2\Pi_{1/2}$ J = 5/2, 7/2 and 9/2 and the $^2\Pi_{3/2}$ J = 5/2 Λ-doubling frequencies, although the accuracy of these, ranging from within 1 - 10kHz, is not so good as from the beam maser. Recently, ter Meulen et al (15) have reported a preliminary investigation of an inverted population of Λ-doublets, using both of these molecular beam methods, in an attempt to understand the maser emission from interstellar OH. The method of preparation of OH for all the aforementioned molecular beam studies has been the reaction of NO_2 with the products of a microwave discharge in water vapour

$$\begin{aligned} H_2O &\longrightarrow H + \text{other products} \\ H + NO_2 &\longrightarrow OH + NO \end{aligned} \qquad (5.18)$$

Double resonance techniques have also been used to obtain high resolution data. Recently, Destombes and Marliere (16) have used a radio-frequency microwave double resonance method to obtain extensive measurements on the $^2\Pi_{3/2}$ J = 7/2 and 9/2 levels, with an accuracy of between 8 and 25kHz.

The Zeeman effect on the rotational energy levels was first investigated by Radford (4, 5) again using a microwave discharge in water vapour to generate the radicals. He was able to determine the effective rotational g-factors for the $^2\Pi_{3/2}$ J = 3/2, 5/2 and 7/2 levels (4) and subsequently for the $^2\Pi_{1/2}$ J = 3/2 and 5/2 levels (5), the linewidths for these experiments varying from 450 to 800kHz. Similar experiments were performed by Clough, Curran and Thrush (17), who detected Λ-doubling transitions arising from within the vibrational levels v = 0 to 4, the method of preparation being

$$H + O_3 \longrightarrow OH + O_2 \qquad (5.19)$$

However, we are only concerned with those transitions arising from the v = 0 level, in which case the results of Radford are to be preferred.

5.4 Measurement of the Zeeman Effect in the $^2\Pi_{3/2}$ J = 9/2 Rotational Levels of OH

These measurements were made in conjunction with Dr. M. Kaise. The method employed to measure the Zeeman effect in the $^2\Pi_{3/2}$ $J = 9/2$ level of OH is basically the same as that used by Radford (4) for the lower rotational levels, namely to observe the Λ-doubling transitions using an e.p.r. spectrometer. From the work of Dousmanis, Sanders and Townes (7) and subsequent workers it is known that the zero field Λ-doubling transitions for the $J = 9/2$ level occur at around 23.8GHz. We have therefore used an e.p.r. spectrometer system operating in the K-band microwave region (18 - 26.5GHz). Choosing an operating frequency reasonably close to that of the zero-field transition frequencies ensures that the magnetic flux density required to tune the relevant energy levels into resonance is within the capabilities of the electromagnet system. Our operating frequency was around 26GHz.

The present experiments differ from those of Radford in only two minor aspects - the method of preparation of OH and the type of cavity used. As regards the preparation of OH, we choose to prepare it by mixing the products of a microwave discharge in CF_4 with water vapour, rather than by the reaction in (5.17). A microwave discharge in CF_4 is known to be a good source of fluorine atoms (18), and so the proposed reaction scheme is

$$\begin{aligned} CF_4 &\longrightarrow F + \text{other discharge products} \\ F + H_2O &\longrightarrow OH + HF \end{aligned} \qquad (5.20)$$

The only alternative preparation we investigated was from a microwave discharge in water vapour, which proved to be slightly inferior. A distinct advantage of the preparation via CF_4 is that since F atoms themselves possess an e.p.r. spectrum (19) readily observable at our operating frequencies, we have a useful method for the initial estimation of optimum relative pressures of CF_4 and water vapour: the F atom signal can be optimised and then titrated out by the addition of water vapour. In practice the optimum OH signals were obtained when the F atom signals were just titrated out. The possibility of monitoring relative pressures of reactants arises also for those reaction schemes involving hydrogen atoms (5.18 or 5.19) but we have found the H atom signal much harder to detect than that of the F atom.

The type of cavity we have used is a confocal resonator system, whereas Radford used a microwave reflection cavity. Both of these types have been discussed in chapter 4. The reason for our use of a confocal resonator is mainly because of the relative volumes of the two types of cavity at K-band frequencies. The volume of a microwave cavity operating in a TE_{011} mode at around 26GHz is approximately $3cm^3$ whereas the internal volume of the confocal resonator is about $100cm^3$. The volume of the former is not really suitable for free radical studies. A larger microwave cavity operating in a higher order mode could be used but we choose to use a confocal resonator since this offers certain other advantages, as discussed in chapter 4. This problem of internal volumes does not arise at the X-band frequencies used by Radford.

The design of the confocal system was based on that for a semi-confocal resonator due to Dr. C.R. Parent. The volume of a semi-confocal cell would be half that of an equivalent confocal cell and for this reason we have used the latter. However, confocal resonators are slightly harder to construct in view of the fact that the coupling hole is drilled through a concave mirror rather than in a plane one. Figure 2 shows a longitudinal section through our confocal cell. The mirrors both have a radius of curvature (R) of 5cm and are 2 inches in diameter. Their separation is difficult to measure in situ but from measurements of the free spectral range $\triangle\nu$ (difference in resonant frequency of successive modes) we can estimate this:

$\triangle\nu$ is measured as ~ 2.87GHz and so from

$$\triangle\nu = \frac{c}{2d}$$

we obtain d as ~ 5.23cm. We can now check the stability of the system, and find the Fresnel number:

$$g_1 = g_2 = 1 - \frac{d}{R} = -0.046$$

Therefore we have $g_1 g_2 = 0.002$ and so from (4.13) the system is stable. The Fresnel number calculated from (4.14) is $N = 1.04$, and so the diffraction losses will be large for all but the TEM_{00} modes, as we required. The dimensions of the cell are of course chosen to meet the stability condition and to give a suitable Fresnel number.

Mechanical tuning of the cavity is possible by adjusting the separation of the mirrors and this is achieved in this case by use of a differential screw system. The cavity was found to be tunable over the entire range of the microwave source - from 18GHz to 26GHz. Edwards O-rings are used to form a vacuum tight system. A section of waveguide is hard-soldered into the body of the upper mirror, and a vacuum seal between this section and the remainder of the waveguide system is formed by use of a Mylar gasket. The

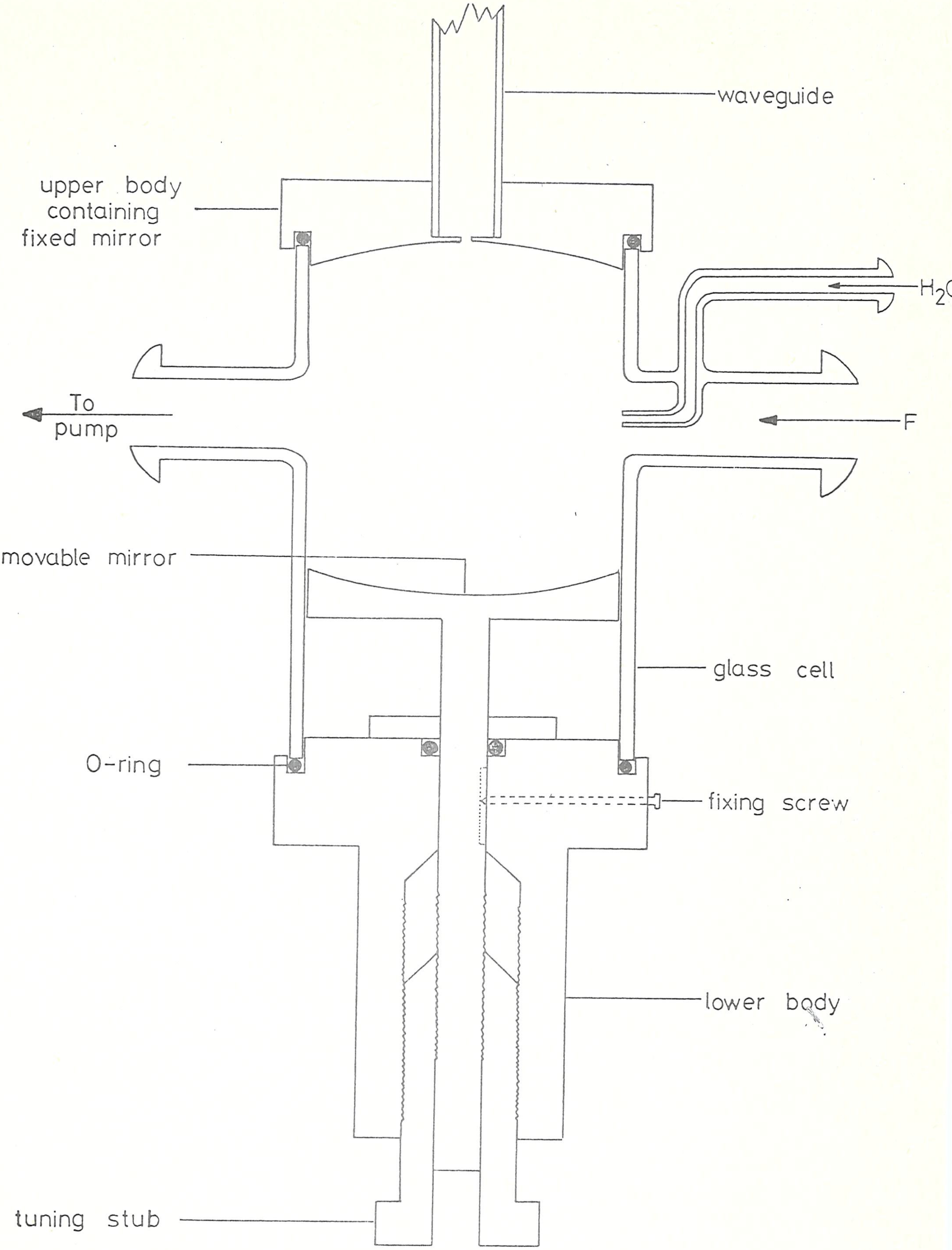


Figure 2 Sketch of confocal resonator used in OH measurements.

cell itself is made of Pyrex glass and since it is required to fit snugly, without leaking and without undue mechanical stress, it follows that the internal diameter and length of the cell are critical. The Zeeman modulation coils are made from 34EN laminated copper wire wound in series on perspex formers fixed externally to the glass cell so as to provide a modulation field parallel to the direction of applied magnetic field. There are four supporting rods in a square arrangement and hence it is possible to arrange the upper body such that all types of magnetic and electric dipole transitions are observable. The OH measurements were made with the upper body orientated such that $\Delta m_J = \pm 1$ electric dipole and $\Delta m_J = 0$ magnetic dipole transitions could be observed. By inserting a 90° twist into the waveguide the upper body can be fitted to the cavity such that $\Delta m_J = \pm 1$ magnetic dipole and $\Delta m_J = 0$ electric dipole transitions could be seen. This is the orientation used for certain measurements on the spectra of atomic fluorine and hydrogen.

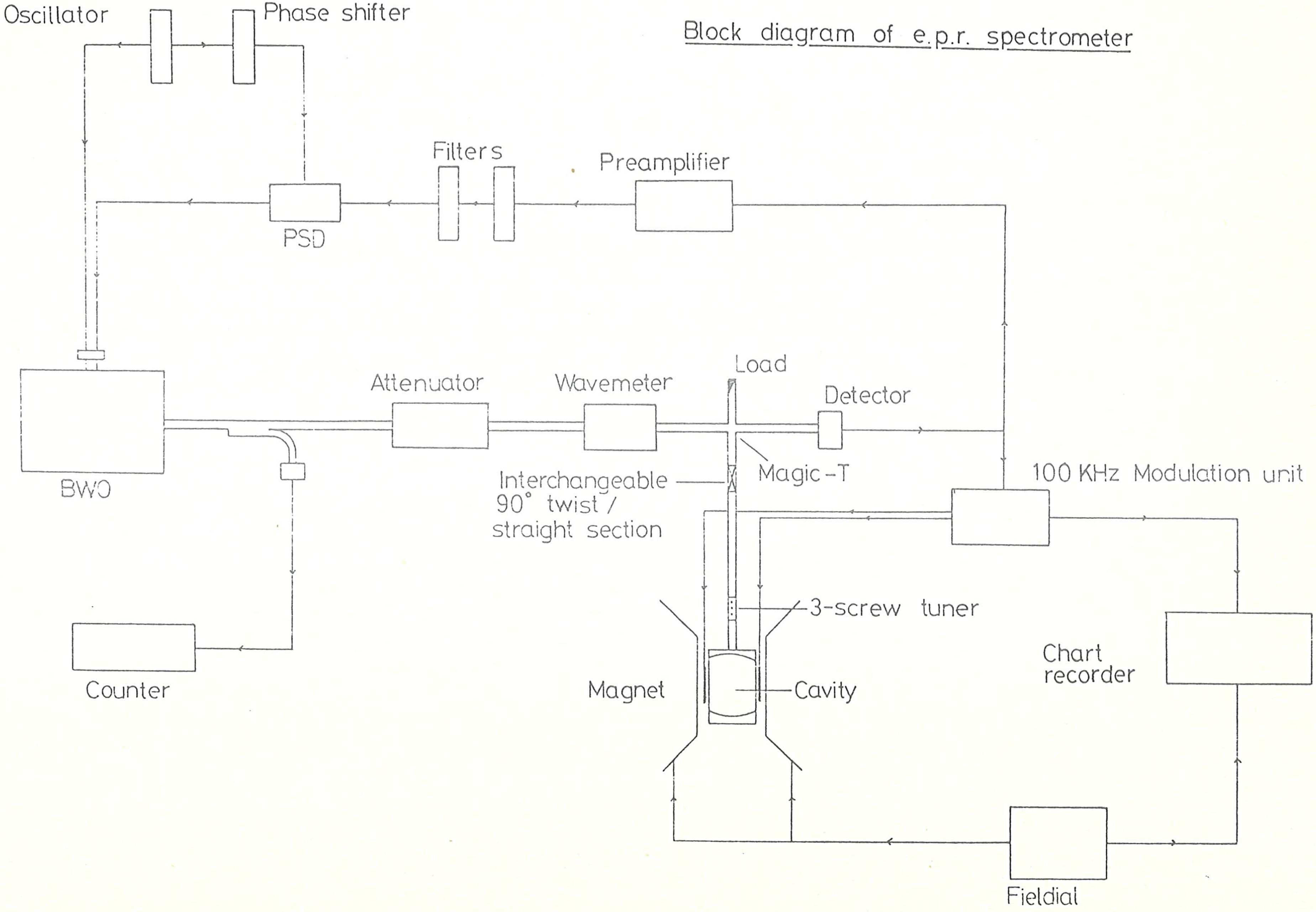
Figure 3 shows the general layout of the spectrometer system. Since this is not a standard system, it will be described in more detail. The microwave source was a Hewlett Packard HP 8690 B backward wave oscillator (BWO). The waveguide system was comprised mainly of components manufactured by Mid-Century Microwavegear Ltd. - the three-screw tuner and certain straight sections were made in the Department of Chemistry workshops. The detector was an MA 493B crystal suitable for the K-band frequency range.

The BWO frequency was locked to the resonant frequency of the cell by an automatic frequency control (AFC) system, using phase sensitive detection. The filters, oscillator, phase shifter and phase sensitive detector (PSD) were manufactured by AIM Electronics Ltd., whereas the preamplifier was a Brookdeal LNA 450. The correction voltage supplied by the AFC system had to be made compatible with the BWO and with this end in mind a circuit, designed by Dr. T.H. Wilmshurst, was connected to the helix input of the BWO.

Modulation was supplied to the Zeeman coils by a Varian 100kHz modulation unit, which also contains its own PSD system. The required absorption signal was recorded from the output of this PSD. The magnetic field was supplied by a Varian V3800 15-inch electromagnet powered by a V-FR2703 power supply, and was regulated and swept by a Fieldial Mk II system. Accurate measurements of the magnetic field at the poleface were made with an AEG magnetometer using a proton resonance probe. The proton resonance frequencies were measured with an AMF Venner digital counter. The frequency of the microwave source was determined using an HP E40-5245L frequency measur-

Figure 3

Block diagram of e.p.r. spectrometer



ing system, which looks the tenth harmonic of a local oscillator frequency to the frequency of the source.

Corrections have to be applied to all of the measured lines because of the difference in magnetic flux densities at the poleface and at the centre of the resonant cell. These corrections were determined by measurement of the spectra of atomic fluorine and hydrogen. The magnetic fields at which the atomic absorption lines occur can be calculated with a high degree of accuracy and by comparison with the measured fields a magnetic field correction curve can be constructed. The field corrections to the measured OH lines are of the order of -1 gauss. The general formula derived by Clendenin (19), as quoted by Radford, Hughes and Beltran-Lopez (20), was used to calculate the field positions of the atomic fluorine lines. This formula gives the energies of the $^2P_{1/2}$ and $^2P_{3/2}$ levels as a function of the applied magnetic field. Since the magnetic field dependence is rather complicated, Radford <u>et al</u> (20) found it convenient to expand a square root in the general formula and hence to derive formulae relevant to individual transitions arising within the $^2P_{3/2}$ levels (transitions from the $^2P_{1/2}$ levels are much weaker and were not observed by Radford <u>et al</u> or by us). The expansion parameter contains quadratic and cubic functions of the magnetic field and hence at high fields the square root expansion is not necessarily valid. In our case, the general formula is to be preferred since our atomic fluorine spectra were recorded at high magnetic fields (approx. 10 kgauss). We have written a computer programme that calculates the field positions of all fluorine atom transitions for a specified operating frequency. This solves the general formula by an iterative procedure, using 3-point equal interval interpolation, which works as follows. We wish to solve

$$\nu = f(H) \qquad (5.21)$$

to find the value of the magnetic field H_0 at a specified frequency ν_{op}. To apply the 3-point equal interval method we must have a range of fields within which we know to be a solution and in addition the solution must be at a turning point in the function. At fairly modest fields (say ~ 3kgauss or more) the energy levels (and hence the transition frequencies) tune almost linearly with field and so there is no turning point in the function f (H). An artificial turning point can be obtained by calculating the <u>absolute</u> deviations from the specified frequency:

$$|\nu - \nu_{op}| = |f(H) - \nu_{op}| = g(H) \qquad (5.22)$$

The function $g\ (H)$ is zero for $\nu = \nu_{op}$ and positive for all other values of ν and hence $g\ (H)$ has a minimum at $\nu = \nu_{op}$. We can therefore solve (5.22) iteratively to find a value for H_0.

The range of search is divided into four intervals by choosing three points, as in figure 4, and the function $g\ (H)$ is evaluated for each of these points. Let the range be a and the field at the midpoint of this range be H_c. The three points will therefore be at $H_c - \frac{1}{4}a$, H_c and $H_c + \frac{1}{4}a$ and the lowest value of $g\ (H)$ will lie within one of three intervals: between $H_c - \frac{1}{2}a$ and H_c; between $H_c - \frac{1}{4}a$ and $H_c + \frac{1}{4}a$; or between H_c and $H_c + \frac{1}{2}a$. The interval containing the lowest value of $g\ (H)$ is retained and the process is repeated. After n iterations the value of H at the minimum of $g\ (H)$ is known with an accuracy of $\pm a(\frac{1}{2})^{n+1}$. We performed twenty iterations with an initial range a of 4000 gauss, which gives a final accuracy of ±0.002 gauss. Table 1 shows the observed and calculated field positions for two of the lines of Radford et al (20) and nine observations made on our 15-inch electromagnet. For comparison the field positions were also calculated using the individual formulae of Radford et al and these two are shown in Table 1. As can be seen, at low fields the results from the formulae of Radford et al are as good as those from the general expression, but at high fields only the general expression gives consistent magnetic field corrections.

The hydrogen atom lines were measured so as to give a correction at lower magnetic fields for the 15-inch magnet system. The field positions were calculated using a programme written by Dr. C.M.L. Kerr. This includes the off-diagonal effects of the Fermi Contact hyperfine interaction.

The gas handling system was constructed entirely of glass, with standard Quickfit joints. Leybold-Heraeus needle valves were used. The vacuum pump was an Edwards ISC 450B with a pumping speed of 555 litres/minute. Gas pressures were estimated using Pirani gauges.

The mixing arrangement of the reactant gases is shown in figure 3. The products of a 2450kHz electrodeless discharge in gaseous CF_4 were pumped straight through the cell. No difficulties were encountered with free electrons, and discharge noise could be reduced by judicious positioning of a damp rag around the discharge cavity. To reduce recombination of fluorine atoms on the walls of the discharge tube the section of tube between discharge and cell was lined with Teflon tubing. Water vapour was admitted to the stream of discharge products through a side arm, the point of mixing being immediately prior to the entrance of the resonant cell.

The optimum signals were recorded using a pressure of 0.5 torr of CF_4

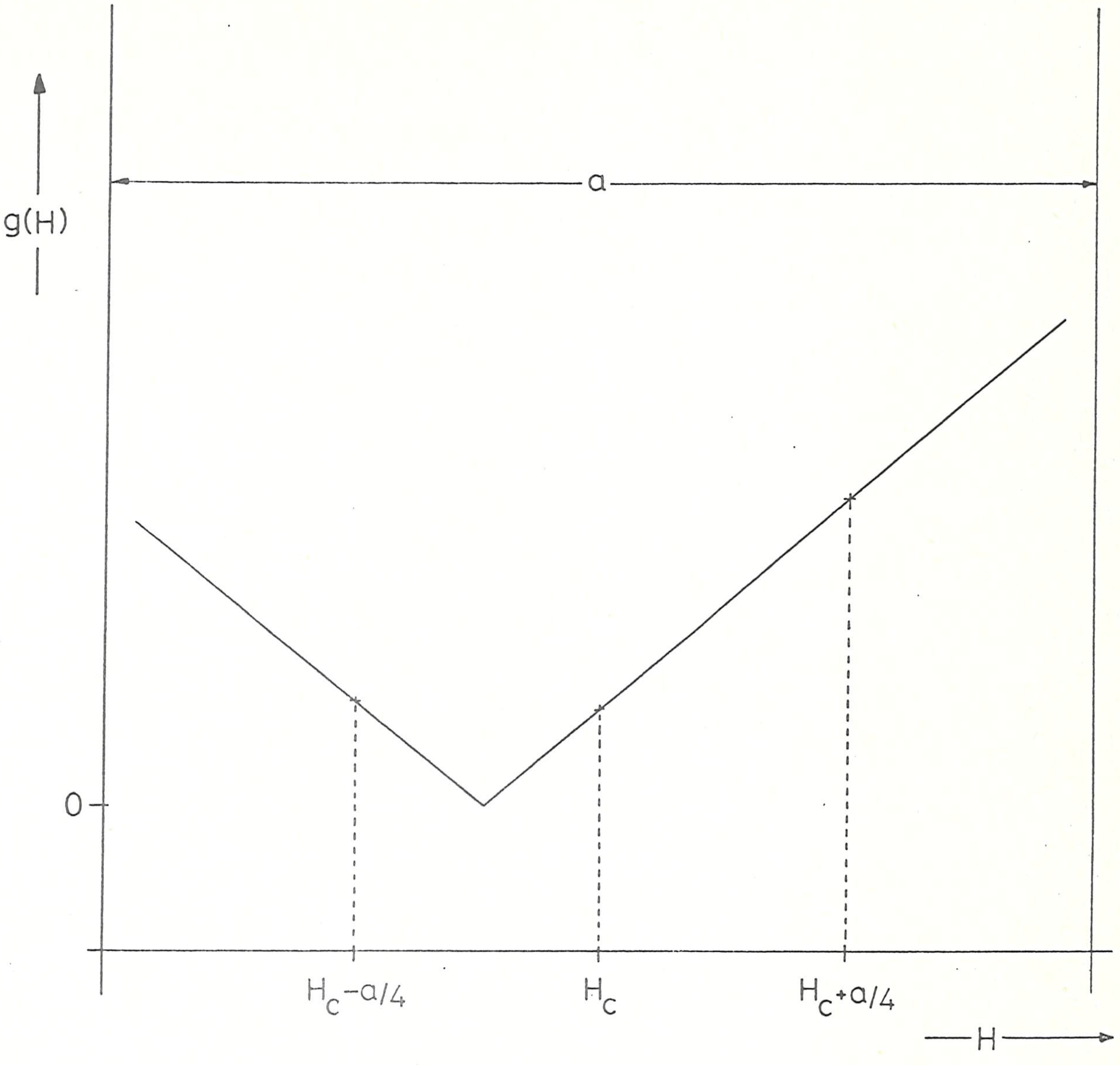


Figure 4 Choice of interpolation points for 3-point equal interval method.

Table 1 Observed and calculated magnetic field positions of atomic fluorine lines.

Operating Frequency (MHz)		Magnetic field (gauss)			
	Observed H_{obs}	Calculated (General formula)		Calculated (Radford's formula)	
		H_1	$H_{obs} - H_1$	H_2	$H_{obs} - H_2$
9103.854[a]	4339.525	4333.462	6.063	4333.587	5.938
9103.854[a]	4432.385	4432.738	-0.353	4432.229	0.156
17157.540[b]	8539.216	8535.749	3.467	8538.171	1.045
17158.040[b]	8636.189	8633.314	2.875	8633.427	2.762
17158.540[b]	8699.722	8697.052	2.670	8694.549	5.173
17160.090[b]	9695.181	9691.932	3.249	9691.893	3.288
17160.220[b]	9749.533	9746.517	3.016	9750.419	-0.886
17159.980[b]	9655.792	9651.298	4.494	9647.394	8.398
20058.019	11216.727	11214.392	2.335	11209.188	7.539
20057.534	11252.264	11249.989	2.275	11249.959	2.305
20057.720	11299.001	11296.845	2.156	11302.048	3.047

a Lines measured by Radford *et al* (20)

b Lines measured by A.J. Pipe (B.Sc. Dissertation, Southampton 1972) and a discharge power of 140 watts. Addition of water vapour to titrate out the atomic fluorine gave a total pressure of around 0.55 torr (in the arm responsible for handling the CF_4). The signal to noise ratio for the strongest lines was then about 20 to 1. For the purpose of measuring line positions lower pressures were used, with a subsequent drop in signal to noise ratio. It was not possible to over-modulate the OH lines and so the spectra were recorded with maximum modulation amplitude. Figure 5 shows the complete spectrum of OH arising from the $^2\Pi_{3/2}$ $J = 9/2$ level. It appears as thirteen lines spread over a range of about 600 gauss. Five of these lines, however, are unresolved hyperfine doublets which gives the total number of lines as eighteen, as expected. Table 2 lists the measured field positions of these lines, the entire spectrum being measured twice. Assignments of these lines will be given in a later section of this chapter. Figure 6 shows the magnetic field correction curve, and it is seen to be almost linear with field. Our OH spectrum lies in the range 6800 to 7300 gauss, the magnetic field correction then ranging from 0.8 to 0.9 gauss respectively. A field correction of 0.85 gauss was applied to all the measured lines - the errors due to taking an average, ± 0.05 gauss, will not cause any serious discrepancies in the analysis since they are much smaller than the linewidth of the observed lines ($\sim$20 gauss, which corresponds to $\sim$7MHz linewidth).

5.5 The Effective Rotational Hamiltonian for $^2\Pi$ Electronic States in the Absence of External Magnetic Fields

Section 5.2 dealt in rather general terms with the theory of the rotational levels of a molecule in a $^2\Pi$ electronic state. The Hamiltonian (5.4) presented in that section was shown to account for various uncoupling phenomena that are particularly important for light molecules such as OH. The problem with this Hamiltonian is that it contains terms off-diagonal in electronic state which make eigenvalue calculations difficult. As discussed in chapter 2, the solution is to construct an effective Hamiltonian that operates only within the $^2\Pi$ manifold. Since these off-diagonal terms are responsible for the uncoupling effects it is essential that these are incorporated into the effective Hamiltonian in the correct manner. This section is concerned with the construction of a suitable effective Hamiltonian, using degenerate perturbation theory,that mimics correctly the effects of the uncoupling terms, and in particular the Λ-doubling terms, since our observed spectra depend so critically on the Λ-doubling intervals. This section is divided into three parts. The first is devoted to

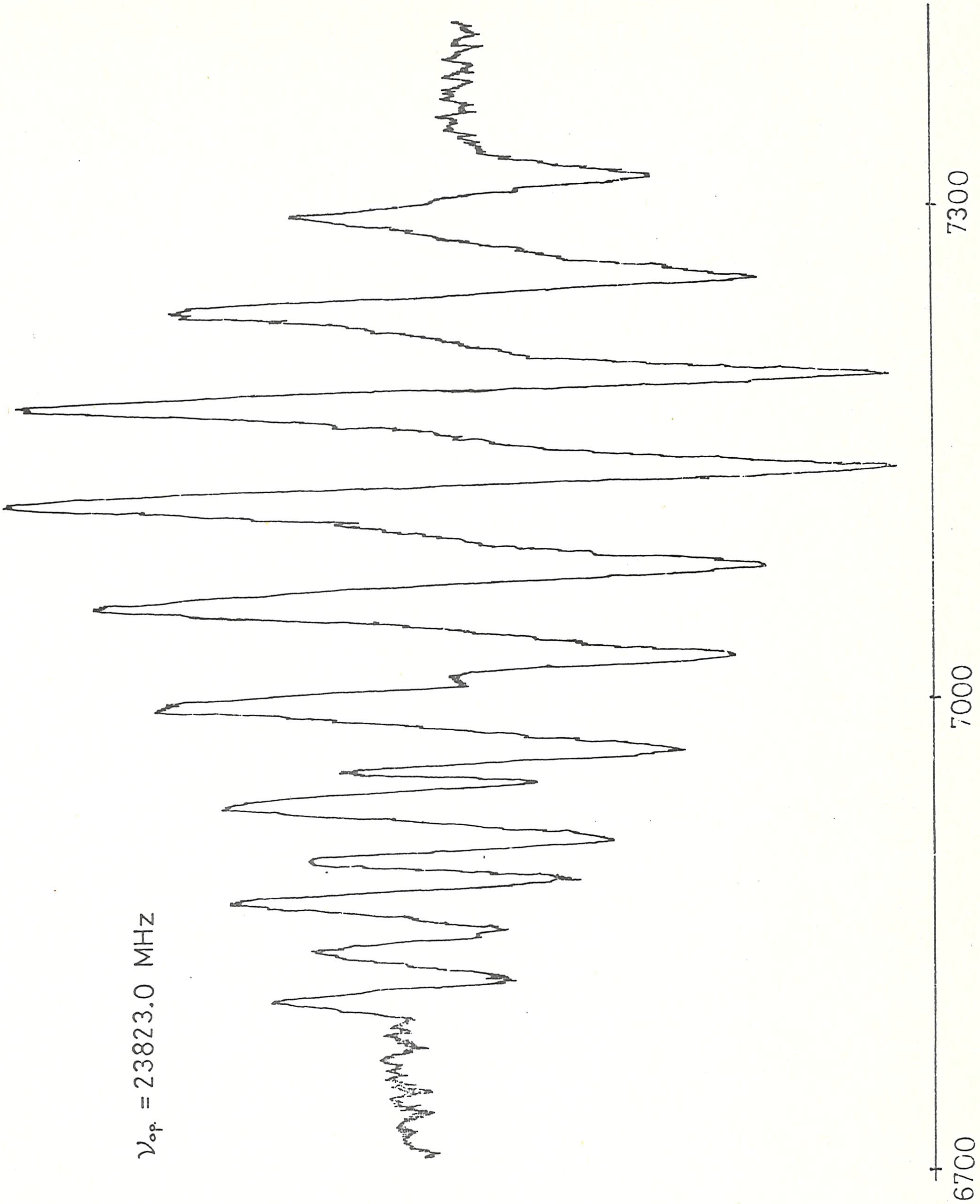


Figure 5 Λ-doubling spectrum arising from ${}^2\Pi_{3/2}$ $J = 9/2$ rotational levels of ^{16}OH.

Table 2 List of Zeeman measurements for $^2\Pi_{3/2}$ J = 9/2 Λ-doubling spectrum.

Line	Frequency (GHz)	Measured Field (gauss)	
1st set			
1	26.25750	6835.95	
2	26.25803	6867.40	
3	26.25837	6897.90	
4	26.25824	6922.35	
5	26.25856	6959.25	
6	26.25850	6978.55	
7	26.25941	7021.20	
8	26.25951	7036.45	
9/10	26.25972	7089.05	Unresolved doublets
11/12	26.25878	7145.25	
13/14	26.25855	7203.25	
15/16	26.25778	7260.95	
17/18	26.25803	7321.55	
2nd set			
1	26.25316	6822.753	
2	26.25322	6853.31	
	26.25345	6853.49	
3	26.25335	6883.67	
4	26.25393	6909.98	
	26.25419	6910.22	
5	26.25426	6946.63	
6	26.25451	6967.14	
7/8	26.25445	7015.28	Unresolved doublets
	26.25832	7026.35	
9/10	26.26210	7097.37	
11/12	26.26258	7156.515	
13/14	26.262667	7216.24	
	26.262670	7216.32	
15/16	26.26279	7276.20	
17/18	26.26314	7335.93	

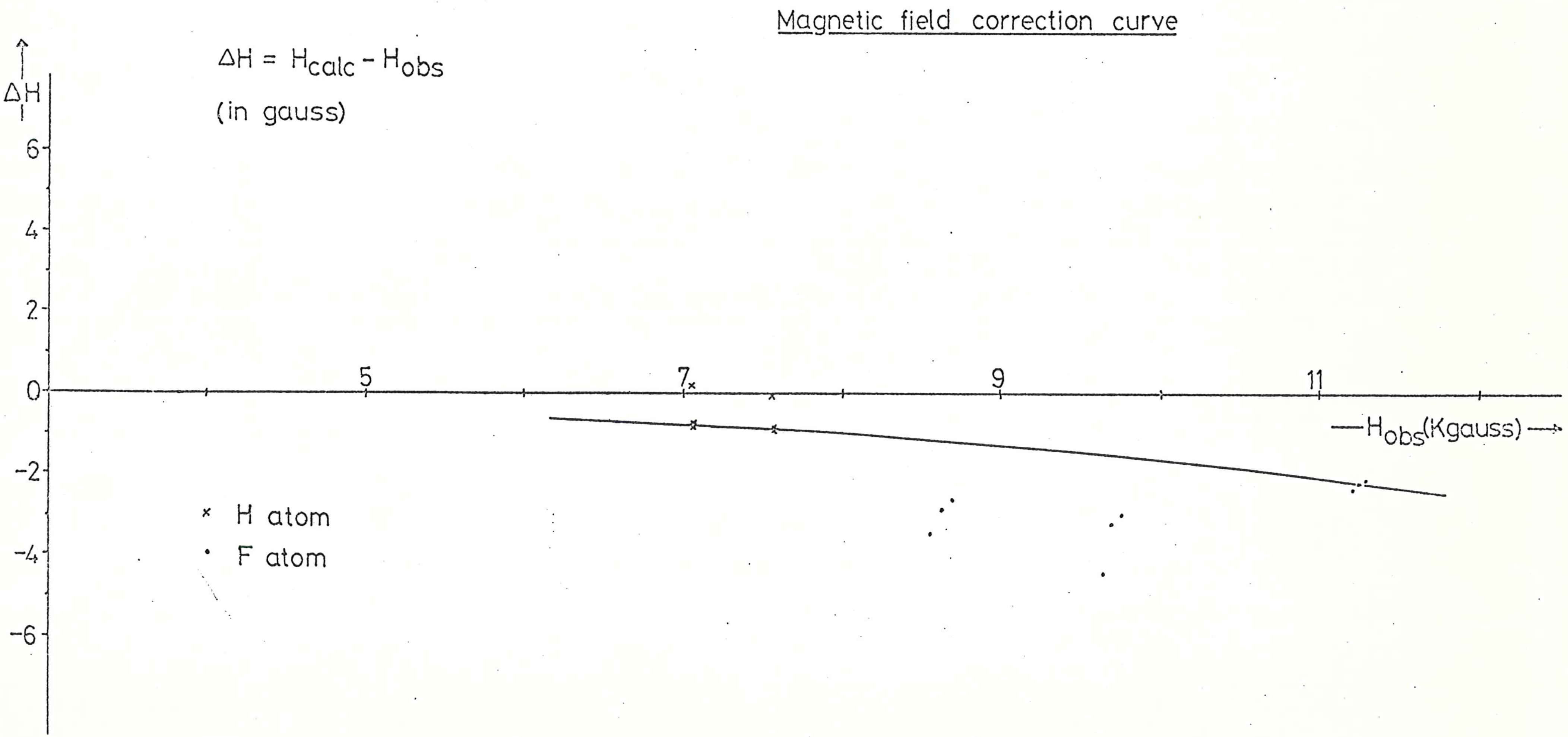

Magnetic field correction curve
$\Delta H = H_{calc} - H_{obs}$
(in gauss)
ΔH
6
4
2
0
-2
-4
-6
5
7
9
11
H_{obs}(Kgauss)
× H atom
• F atom

Figure 6.

a derivation of a second order effective Hamiltonian containing the dominant Λ-doubling interactions. The hyperfine interactions are also included here. The second part deals with centrifugal distortion corrections and the third with some small third-order corrections to the hyperfine Hamiltonian. The basis states used in this section are non-paritised basis functions.

Second Order Effective Hamiltonian

The Hamiltonian for the spin-orbit and rotational interactions has been given in equation (5.4) as

$$H = AT^1(\underline{L}).\,T^1(\underline{S}) + BT^1(\underline{J}-\underline{L}-\underline{S}).\,T^1(\underline{J}-\underline{L}-\underline{S})$$

This Hamiltonian contains terms both diagonal and off-diagonal in electronic state, but we require a Hamiltonian that operates only on ${}^2\Pi(v = 0)$ vibronic wavefunctions. As has been discussed in chapter 2, in order to apply the methods of degenerate perturbation theory to obtain an effective rotational Hamiltonian, the total Hamiltonian H_T has to be partitioned in the following manner:

$$H_T = H_0 + \lambda$$

The eigenfunctions of H_0, the vibronic Hamiltonian, are pure ${}^2\Pi$ wavefunctions, i.e. adiabatic states. V describes the rotational interactions and contains the non-adiabatic terms responsible for the admixture of other electronic states. In this case, therefore, the perturbation V is taken to be the Hamiltonian (5.4).

The first order effective rotational Hamiltonian is given by those terms in (5.4) that are diagonal in electronic state. By inspection of equation (5.6), the expansion of (5.4), these terms are found to be:

$$\begin{aligned} H^{(1)}_{\rm eff} &= P_0VP_0 \\ &= A\Lambda\Sigma + B\left[J(J+1) + S(S+1) - \Omega^2 - \Sigma^2\right] \\ &\qquad - 2B\sum_q{}^{\dagger}(-1)^q\,T^1_q(\underline{J})\,T^1_{-q}(\underline{S}) \qquad (5.23) \end{aligned}$$

The effects of these interactions on the rotational energy levels has been discussed in section 5.2. We merely note that there are no terms in the first order Hamiltonian responsible for Λ-doubling - for these we have to go to higher orders of perturbation theory.

The second order effective Hamiltonian arises from those terms in (5.6) that have matrix elements between electronic states - these are the terms involving $T^1_{\pm 1}(\underline{L})$. We shall ignore the term $B \sum_q^\dagger (-1)^q \, T^1_q(\underline{L}) \, T^1_{-q}(\underline{L})$ since this gives a constant shift to all the rotational levels and so to second order can only lead to terms mimicking interactions that are already present. The only terms that have to be considered are the L-uncoupling terms and those uncoupling $\underline{S}$ from $\underline{L}$. These we shall denote V_1 and V_2 respectively. Hence

$$\begin{aligned} V_1 &= -2B \sum_q^\dagger (-1)^q \, T^1_q(\underline{J}) \, T^1_{-q}(\underline{L}) \\ V_2 &= (A + 2B) \sum_q^\dagger (-1)^q \, T^1_q(\underline{L}) \, T^1_{-q}(\underline{S}) \end{aligned} \qquad (5.24)$$

The interactions arising in second order are of the form

$$\begin{aligned} H^{(2)}_{\text{eff}} &= \lambda^2 \, P_0 V \, (Q_0/a) \, V P_0 \\ &= \sum_{\eta''\Lambda''S''} \frac{\langle {}^2\Pi | V_1 + V_2 | \eta''\Lambda''S'' \rangle \langle \eta''\Lambda''S'' | V_1 + V_2 | {}^2\Pi \rangle}{(E^0_{{}^2\Pi} - E^0_{\eta''\Lambda''S''})} \\ &= \sum_{\eta''\Lambda''S''} (E^0_{{}^2\Pi} - E^0_{\eta''\Lambda''S''})^{-1} \Big\{ \langle {}^2\Pi | V_1 | \eta''\Lambda''S'' \rangle \langle \eta''\Lambda''S'' | V_1 | {}^2\Pi \rangle \\ &\quad + 2 \langle {}^2\Pi | V_1 | \eta''\Lambda''S'' \rangle \langle \eta''\Lambda''S'' | V_2 | {}^2\Pi \rangle \\ &\quad + \langle {}^2\Pi | V_2 | \eta''\Lambda''S'' \rangle \langle \eta''\Lambda''S'' | V_2 | {}^2\Pi \rangle \Big\} \end{aligned} \qquad (5.25)$$

where the summation is over all electronic states $|\eta''\Lambda''S''\rangle$ excluding the $^2\Pi$ state for which the effective Hamiltonian is required. Rotational quantum numbers have been suppressed in the above, their presence being taken as understood.

Consider the three items within the brackets in more detail. The first of these is, explicitly,

$$\begin{aligned} &\langle {}^2\Pi ; \Lambda S \Sigma J \Omega M | -2B \sum_{q_1}^\dagger (-1)^{q_1} \, T^1_{q_1}(\underline{J}) \, T^1_{-q_1}(\underline{L}) | \eta''\Lambda''S''\Sigma''J''\Omega''M'' \rangle \\ &\times \langle \eta''\Lambda''S''\Sigma''J''\Omega''M'' | -2B \sum_{q_2}^\dagger (-1)^{q_2} \, T^1_{q_2}(\underline{J}) \, T^1_{-q_2}(\underline{L}) | {}^2\Pi ; \Lambda' S \Sigma' J' \Omega' M' \rangle \end{aligned} \qquad (5.26)$$

where q_2 can take the values $\pm q_1$. Since $T^1(\underline{S})$ operates only on the rotational part of the basis functions and $T^1(\underline{L})$ on the electronic part, (5.26) can be factorised to give

$$\sum_{q_1 q_2}^{\dagger} \left\{ 4 \langle {}^2\Pi, \Lambda \mid BT^1_{-q_1}(\underline{L}) \mid \eta''\Lambda''S'' \rangle \langle \eta''\Lambda''S'' \mid BT^1_{-q_2}(\underline{L}) \mid {}^2\Pi, \Lambda' \rangle \right\}$$

$$\times \langle J\Omega M \mid T^1_{q_1}(\underline{J}) \mid J''\Omega''M'' \rangle \langle J''\Omega''M'' \mid T^1_{q_2}(\underline{J}) \mid J'\Omega'M' \rangle \qquad (5.27)$$

Equation (5.25) contains an implicit summation over J", Ω" and M" and so the closure relationship

$$\sum_{J''\Omega''M''} \mid J''\Omega''M'' \rangle \langle J''\Omega''M'' \mid \;=\; 1 \qquad (5.28)$$

can be used to simplify (5.25):

$$\sum_{q_1 q_2}^{\dagger} X_{q_1 q_2} \quad \langle J\Omega M \mid T^1_{q_1}(\underline{J})\; T^1_{q_2}(\underline{J}) \mid J'\Omega'M' \rangle \qquad (5.29)$$

where $X_{q_1 q_2}$ is the electronic factor contained in brackets in equation (5.27).

If $q_2 = -q_1$ in (5.29) the rotational matrix element is then of the same form as the off-diagonal matrix elements of $T^1(\underline{J}) . T^1(\underline{J})$ and hence this term can be absorbed into the first order rotational Hamiltonian. The factor containing the electronic matrix elements

$$\sum_{\eta''\Lambda''S''} \left(E^0_{{}^2\Pi} - E^0_{\eta''\Lambda''S''}\right)^{-1} \;\; 4 \langle {}^2\Pi, \Lambda \mid BT^1_{-q_1}(\underline{L}) \mid \eta''\Lambda''S'' \rangle$$

$$\times \; \langle \eta''\Lambda''S'' \mid BT^1_{q_1}(\underline{L}) \mid {}^2\Pi, \Lambda' \rangle$$

obtained from (5.25) and (5.27) can be regarded as a constant. We note that both Σ and Δ states are mixed into the ${}^2\Pi$ state by the $T^1_{\pm 1}(\underline{L})$ operator and in addition that we must have $\Lambda' = \Lambda$, since

$$\Lambda' = \Lambda'' - q_1 = (\Lambda + q_1) - q_1 = \Lambda .$$

This second order term is therefore not responsible for lifting the Λ-degeneracy.

However, if we consider $q_2 = q_1$ in the same manner we obtain a second order interaction of the form

$$\begin{aligned} \Bigg\{ \sum_{\eta''\Lambda''S''} & (E^0_{{}^2\Pi} - E^0_{\eta''\Lambda''S''})^{-1} \; 4\langle {}^2\Pi, \Lambda | BT^1_{-q_1}(\underline{L}) | \eta''\Lambda''S'' \rangle \\ & \times \; \langle \eta''\Lambda''S'' | BT^1_{-q_1}(\underline{L}) | {}^2\Pi, \Lambda' \rangle \Bigg\} \\ & \times \; \langle J\Omega M | T^1_{q_1}(\underline{J}) \, T^1_{q_1}(\underline{J}) | J'\Omega' M' \rangle \end{aligned} \qquad (5.30)$$

Examination of the electronic matrix elements reveals that this interaction mixes states of different Λ since we have

$$\langle {}^2\Pi \; \Lambda = \pm 1 | T^1_{\pm 1}(\underline{L}) | \Lambda'' = 0 \rangle \langle \Lambda'' = 0 | T^1_{\pm 1}(\underline{L}) | {}^2\Pi \; \Lambda' = \mp 1 \rangle$$

i.e. $\Delta\Lambda = \mp 2$.

This term therefore describes a Λ-doubling phenomenon, which in second order of perturbation theory arises solely from the admixture of excited Σ states. The expression within braces is again regarded as a constant; this can be identified with the $\underline{q}$ parameter of Mulliken and Christy (20) or the β parameter of Dousmanis, Sanders and Townes (7), the relation between these being

$$\underline{q} \; = \; -2\beta \; = -8 \sum_{\Sigma \text{ states}} \frac{|\langle {}^2\Pi | BL_y | \Sigma \rangle|^2}{E_\Sigma - E_{{}^2\Pi}} \qquad (5.31)$$

We shall use the $\underline{q}$ parameter.

In our spherical tensor notation we therefore have

$$\underline{q} \; = \; -4 \sum_{\Sigma \text{ states}} \frac{|\langle {}^2\Pi | BT^1_{-q}(\underline{L}) | \Sigma \rangle|^2}{E^0_{{}^2\Pi} - E^0_\Sigma}$$

The effective Λ-doubling Hamiltonian derived from (5.30) is

$$H_{LD}\,(V_1^2) \; = \; \underline{q} \sum_q{}^{\dagger} (-1)^q \; T^1_q(\underline{J}) \; T^1_q(\underline{J}) \qquad (5.32)$$

where we have arbitrarily introduced a phase factor $(-1)^q$ so as to be consistent with equation (2.33). The matrix elements of this Hamiltonian are

$$\langle {}^2\Pi(\Lambda = \pm 1);\ S\Sigma J\Omega M | H_{LD}\ (V_1^2) | {}^2\Pi(\Lambda = \mp 1);\ S\Sigma' J'\Omega' M' \rangle$$

$$= \underline{q} \sum_q{}^{\dagger} (-1)^q\ (-1)^{J-\Omega+J-\Omega''} \begin{pmatrix} J & 1 & J \\ -\Omega & -q & \Omega'' \end{pmatrix} \begin{pmatrix} J & 1 & J \\ -\Omega'' & -q & \Omega' \end{pmatrix} J(J+1)(2J+1)$$

$$\times\ \delta_{JJ'}\ \delta_{MM'}\ \delta_{\Sigma\Sigma'} \qquad (5.33)$$

The sum rules on the components of the 3-j symbols show that $\Omega' = \Omega \pm 2$ and hence the Hamiltonian (5.32) mixes fine structure states with $\Omega = \pm 3/2$ into those with $\Omega = \mp 1/2$.

This process can be repeated for the other two terms in (5.25). From the term involving both V_1 and V_2 a further Λ-doubling interaction arises, which is of the form

$$H_{LD}\ (V_1V_2) = -(\underline{p + 2q}) \sum_q{}^{\dagger} (-1)^q\ T_q^1(\underline{J})\ T_q^1(\underline{S}) \qquad (5.34)$$

where $(\underline{p + 2q})$ is a Λ-doubling parameter introduced by Mulliken and Christy. In our notation

$$\underline{(p + 2q)} = 8 \sum_{\Sigma \text{ states}} \frac{\langle {}^2\Pi | (A+2B)\ T_{-q}^1(\underline{L}) | \Sigma \rangle \langle \Sigma | BT_{-q}^1(\underline{L}) | {}^2\Pi \rangle}{(\ E_{^2\Pi}^0 - E_{\Sigma}^0\ )}$$

$$(5.35)$$

This is related to Dousmanis *et al*'s α parameter

$$(\underline{p + 2q}) = -2\alpha$$

Once again we note that to second order, only excited Σ states are responsible for the Λ-doubling in Π states. The matrix elements of (5.34) are as follows:

$$\langle {}^2\Pi(\Lambda = \pm 1);\ S\Sigma J\Omega M | H_{LD}\ (V_1V_2) | {}^2\Pi(\Lambda = \mp 1);\ S\Sigma' J'\Omega' M' \rangle$$

$$= -(\underline{p + 2q}) \sum_q{}^{\dagger} (-1)^{J-\Omega+S-\Sigma} \begin{pmatrix} J & 1 & J \\ -\Omega & q & \Omega' \end{pmatrix} [J(J+1)(2J+1)]^{\frac{1}{2}}$$

$$\times \begin{pmatrix} S & 1 & S \\ -\Sigma & -q & \Sigma' \end{pmatrix} [S(S+1)(2S+1)]^{\frac{1}{2}}\ \delta_{JJ'}\ \delta_{MM'} \qquad (5.36)$$

This Hamiltonian has matrix elements between states subject to $\Delta\Omega = \pm 1$ and $\Delta\Sigma = \mp 1$ and hence in $^2\Pi$ states connects $\Omega = +\frac{1}{2}$ with $\Omega = -\frac{1}{2}$ states.

An interaction diagonal in Λ also arises from the V_1V_2 term, but this has the same form as the spin-uncoupling (or spin-rotation) parameter and is therefore a second order correction to B (or γ).

The third term in (5.25) gives rise to matrix elements containing the pair of 3-j symbols

$$\begin{pmatrix} S & 1 & S \\ -\Sigma & q_1 & \Sigma'' \end{pmatrix} \begin{pmatrix} S & 1 & S \\ -\Sigma'' & q_2 & \Sigma' \end{pmatrix}$$

If $q_1 = q_2 = q$, the sum rules show that $\Delta\Sigma = 2q = \pm 2$. These matrix elements therefore vanish for $^2\Pi$ states since the only possible values for are $+\frac{1}{2}$ and $-\frac{1}{2}$. This Λ -doubling term (Mulliken and Christy parameter $\underline{o}$) has non-zero matrix elements only for states of multiplicity greater than doublet. This is readily appreciated by contraction of these 3-j symbols using equation (2.39), which leads to an expression involving the product of three Wigner n-j symbols:

$$\begin{Bmatrix} 1 & S & S \\ S & 1 & 2 \end{Bmatrix} \begin{pmatrix} 1 & 1 & 2 \\ q & q & -2q \end{pmatrix} \begin{pmatrix} S & S & 2 \\ \Sigma' & -\Sigma & 2q \end{pmatrix}$$

Examination of the triangle rules on, say, the final 3-j symbol reveals that this term is non-zero only for $S \geqslant 1$, i.e. for triplet or higher multiplicities.

The same is not true for the case where $q_1 = -q_2$. This term gives rise to spin-spin interactions which are diagonal in all quantum numbers. For doublet states only the scalar spin-spin interaction is present and this imparts a constant shift to all the rotational levels. We are justified in ignoring this term completely for $^2\Pi$ states.

The derivation of a second order effective Hamiltonian has been shown to lead to two additional terms, both of which account for the phenomenon of Λ -doubling, and both of which arise from the admixture of excited Σ states. In the case of OH, the lowest excited state is a $^2\Sigma^+$ state roughly 32000cm^{-1} higher in energy than the $X^2\Pi$ state. We therefore expect the Λ -doubling in OH to arise predominantly from mixing with this state.

The complete second order effective Hamiltonian in the absence of external fields is taken to be

$$H = H_{RSO} + H_{LD} + H_{hfs} \qquad (5.37)$$

H_{RSO} is the Hamiltonian for rotational motion and spin-orbit coupling, as given in equation (5.23). H_{LD} is the Λ-doubling Hamiltonian and is given in equations (5.32) and (5.34). H_{hfs} is the hyperfine Hamiltonian which is necessary to account for interactions with the nuclear spin angular momentum $\underline{I}$ of the hydrogen atom. We define this along the lines of Carrington, Levy and Miller (22):

$$\begin{aligned} H_{hfs} = \mu_B g_N \mu_N T^1(\underline{I}) \cdot \Big[& \frac{2}{\langle r^3 \rangle} T^1(\underline{L}) \\ & + \frac{8\pi}{3} g_S \langle \delta(\underline{r}) \rangle T^1(\underline{S}) + \sqrt{30}\, g_S T^1(\underline{S}, \underline{C}^2) \Big] \\ & + d \sum_q{}^{\dagger} T^1_q(\underline{S})\, T^1_q(\underline{I}) \end{aligned} \qquad (5.38)$$

where $T^1_{-q}(\underline{S}, \underline{C}^2) = \sum_{q_1 q_2} (-1)^q T^1_{q_1}(\underline{S}) \begin{pmatrix} 1 & 2 & 1 \\ q_1 & q_2 & q \end{pmatrix} \langle C^2_{q_2}(\theta, \phi)\, r^{-3} \rangle$;

$C^2_{q_2}(\theta, \phi)$ is a spherical harmonic;

$\underline{r}$ is a vector describing the separation of hydrogen nucleus and the unpaired electron.

The first term in (5.38) describes nuclear spin/electronic orbital interaction, the second the Fermi contact interaction, the third the nuclear spin/electron spin dipolar term, which could also be written in the form $T^2(\underline{I}, \underline{S})$, and the final term is a Λ-doubling hyperfine interaction. We find it convenient to keep these four terms separated, since then the parameters describing them give direct information on the molecular quantities, such as unpaired electron density at the nucleus $\langle \delta(\underline{r}) \rangle$. The hyperfine parameters we therefore define as follows:

$$\frac{2}{\langle r^3 \rangle} g_S \mu_B g_N \mu_N = a$$

$$\frac{8\pi}{3} g_S \mu_B g_N \mu_N \langle \delta(\underline{r}) \rangle = \alpha'$$

$$\frac{1}{2} g_S \mu_B g_N \mu_N \langle C^2_0(\theta, \phi)\, r^{-3} \rangle = \beta'' \qquad (5.39)$$

and d remains as d.

The a and d parameters are identical to the a and d hyperfine parameters defined by Frosch and Foley (23). The α' and β'' parameters are defined in accordance with Carrington, Levy and Miller (24) and can be related to the Frosch and Foley b and c parameters:

$$\alpha' = \tfrac{1}{3}(3b + c)$$
$$\beta'' = \tfrac{1}{3}c \qquad (5.40)$$

The matrix elements of the complete second order Hamiltonian (3.57) will not be given here. They are readily obtained using standard spherical tensor techniques. Note that the basis functions $|\eta\Lambda;\, S\Sigma;\, J\Omega M\rangle$ used in section (5.2) cannot be used to calculate hyperfine matrix elements since they contain no nuclear spin wavefunctions. There are two choices of basis set involving nuclear spin functions - a coupled set and a decoupled set. In the former we define a grand total angular momentum $\underline{F}$,

$$\underline{F} = \underline{J} + \underline{I}$$

as described in section (5.2) and the basis set in this case is

$$|\eta\Lambda;\, S\Sigma;\, J\Omega I F m_F\rangle$$

m_F relates to the space-fixed component of F and is a good, i.e. well-defined, quantum number. In the decoupled scheme $\underline{J}$ and $\underline{I}$ are not coupled together, the basis set now being

$$|\eta\Lambda;\, S\Sigma;\, J\Omega m_J;\, I m_I\rangle$$

m_I relates to the space-fixed component of I. m_J and m_I are not good quantum numbers but their sum, m_F, remains well-defined:

$$m_I + m_J = m_F$$

Centrifugal Distortion Terms

The second order effective Hamiltonian that we have derived so far operates solely within the $^2\Pi$ electronic state, and contains terms describing the rotational motion and Λ-doubling. We can go further than this and derive an effective Hamiltonian that operates only within a single vibronic state. Additional terms appear in this Hamiltonian that describe the effects of centrifugal distortion. The major contribution to the centrifugal distortion arises from the admixture of other vibrational states, although there is a minor contribution arising from mixing of electronic states. These terms are best treated by a perturbation procedure, taking the above second order Hamiltonian as the perturbation V.

Suppose we take the rotational terms in this Hamiltonian to second order. The matrix element becomes, for the vibrational contribution ,

$$H^{(2)}_{\mathrm{eff}} = P_0 V \,(Q_0/a)\, V P_0$$

$$= \sum_{v'\neq 0} \; \sum_{\Sigma''J''\Omega''M''} (E^0_{v=0} - E^0_{v'})^{-1}$$

$$\times \langle {}^2\Pi;\ v=0; \Lambda S \Sigma J \Omega M | B T^1(\underline{J}-\underline{L}-\underline{S}).T^1(\underline{J}-\underline{L}-\underline{S}) | {}^2\Pi;\ v'; \Lambda S \Sigma''J''\Omega''M'' \rangle$$

$$\times \langle {}^2\Pi;\ v'; \Lambda S \Sigma''J''\Omega''M'' | B T^1(\underline{J}-\underline{L}-\underline{S}).T^1(\underline{J}-\underline{L}-\underline{S}) | {}^2\Pi;\ v=0; \Lambda S \Sigma'J'\Omega'M' \rangle$$

(5.41)

B is a function of the internuclear separation, R, and hence is also a function of the vibrational quantum number v. Equation (5.41) can therefore be factorised into a vibrational part, containing B, and a rotational part. This leads to a term of the form

$$\sum_{v''\neq 0} \frac{|\langle v=0|B|v''\neq 0\rangle|^2}{(E^0_{v=0} - E^0_{v''})}$$

$$\times \sum_{\gamma''} \langle \Lambda S \Sigma J \Omega M | T^1(\underline{J}-\underline{L}-\underline{S}).T^1(\underline{J}-\underline{L}-\underline{S}) | \Lambda S \Sigma''J''\Omega''M'' \rangle$$

$$\times \langle \Lambda S \Sigma''J''\Omega''M'' | T^1(\underline{J}-\underline{L}-\underline{S}).T^1(\underline{J}-\underline{L}-\underline{S}) | \Lambda S \Sigma'J'\Omega'M' \rangle \qquad (5.42)$$

where γ'' represents the double-primed rotational and spin quantum numbers. This equation is identical to the usual centrifugal distortion correction to the rotation of the nuclei:

$$- D_B \langle S \Sigma J \Omega M | (T^1(\underline{J}-\underline{L}-\underline{S}).T^1(\underline{J}-\underline{L}-\underline{S}))$$

$$\times (T^1(\underline{J}-\underline{L}-\underline{S}).T^1(\underline{J}-\underline{L}-\underline{S})) | S \Sigma'J'\Omega'M' \rangle$$

and so we can identify D_B with the vibrational terms in (5.42)

$$D_B = - \sum_{v''\neq v} \frac{|\langle v|B|v''\rangle|^2}{(E^0_v - E^0_{v''})} \qquad (5.43)$$

This is well known (25). A similar treatment for the electronic contributions leads to an expression of the same form as (5.42) but with a parameter given by

$$D_B^{el} = - \sum_{\eta''\Lambda''S''} \frac{|\langle {}^2\Pi|B|\eta''\Lambda''S''\rangle|^2}{(E^0_{{}^2\Pi} - E^0_{\eta''\Lambda''S''})} \qquad (5.44)$$

The matrix elements in (5.42) are non-zero since the electronic wavefunctions are also functions of R. D_B^{el} is a small correction to the vibrational contribution to D_B given in (5.43). The matrix elements of D_B will not be presented here.

We now go on to consider centrifugal distortion corrections to the spin-orbit coupling. These have been treated by James (26) who suggested the introduction of a parameter A_J to describe these corrections. Veseth (27) subsequently showed by a perturbation treatment that A_J could be written in the form

$$A_J = \sum_{v''\neq v} \frac{\langle v|B|v''\rangle\langle v''|A|v\rangle}{E^0_v - E^0_{v''}} \qquad (5.45)$$

where the matrix element involving A is non-zero because A is a function of R. The energy corrections arising from this term are indistinguishable from those arising from the spin-rotation interaction and so it is only necessary to include one of these terms in the effective Hamiltonian. We choose to include a spin-rotation term (of form $\gamma \sum_q^{\dagger} T^1_q(\underline{J})\, T^1_{-q}(\underline{S})$), but it must be remembered that the experimentally determined parameter is then a linear combination of γ and A_J. It is possible to obtain individual values for these parameters and Brown and Watson (28) have suggested the use of isotope dependences to determine them. These authors have pointed out that earlier methods of separation of these parameters are based on incorrect assumptions.

Corrections to the Λ-doubling due to centrifugal distortion can be treated in a similar manner. These arise from cross-terms between the Λ-doubling and rotational Hamiltonians, and once again the possibility of both vibrational and electronic contributions arises. We shall concern ourselves here with the vibrational corrections since these are expected to be the larger. The electronic contributions have been treated by Meerts and Dymanus (29) using a third order perturbation procedure, and we shall compare our results with theirs in the next section.

We shall treat the Λ-doubling Hamiltonian, H_{LD}, developed earlier in this section as part of the perturbation Hamiltonian, V, since the centrifugal distortion corrections then arise in second order of perturbation theory. These have the form

$$\sum_{\substack{\gamma'' \\ v''\neq v}} \frac{\langle v; \gamma | H_{LD} | v''; \gamma'' \rangle \langle v''; \gamma'' | H_{ROT} | v; \gamma' \rangle}{E_v^0 - E_{v''}^0} \qquad (5.46)$$

where γ signifies the set of spin and rotational quantum numbers. Since H_{LD} and H_{ROT} do not commute the Hermitian average of (5.46) has to be taken. This point will be returned to later. We note that since H_{LD} is itself a second order perturbation term, the centrifugal distortion corrections arising from this calculation are really to be regarded as third order terms.

Consider, first of all, the terms from H_{LD} responsible for mixing the fine structure states - these involve the parameter $\underline{q}$. Substitution of (5.32) into (5.46), together with the rotational part of (5.4) leads to

$$\sum_{\substack{\gamma'' \\ v''\neq v}} (E_v^0 - E_{v''}^0)^{-1}$$

$$\times \langle {}^2\Pi; v; \gamma | \sum_q{}^{\dagger} (-1)^q \, \underline{q} \, T_q^1(\underline{J}) \, T_q^1(\underline{J}) | {}^2\Pi; v''; \gamma'' \rangle$$

$$\times \langle {}^2\Pi; v''; \gamma'' | \sum_{q'} (-1)^{q'} \, B T_{q'}^1(\underline{J}-\underline{L}-\underline{S}) \, T_{-q'}^1(\underline{J}-\underline{L}-\underline{S}) | {}^2\Pi; v; \gamma' \rangle \qquad (5.47)$$

This can be factorised to give

$$D_q \sum_{\gamma''} \langle {}^2\Pi; \gamma | \sum_q{}^{\dagger} (-1)^q \, T_q^1(\underline{J}) \, T_q^1(\underline{J}) | {}^2\Pi; \gamma'' \rangle$$

$$\times \langle {}^2\Pi; \gamma'' | \sum_{q'} (-1)^{q'} \, T_{q'}^1(\underline{J}-\underline{L}-\underline{S}) \, T_{-q'}^1(\underline{J}-\underline{L}-\underline{S}) | {}^2\Pi; \gamma' \rangle \qquad (5.48)$$

where D_q is defined by analogy with D_B and is given by

$$D_q = \sum_{v''\neq v} \frac{\langle v | \underline{q} | v'' \rangle \langle v'' | B | v \rangle}{(E_v^0 - E_{v''}^0)} \qquad (5.49)$$

If we now take a Hermitian average and case expression (5.48) into an operator equivalent form we obtain:

$$H_{D_q} = \tfrac{1}{2}D_q \sum_q{}^{\dagger} (-1)^q \Big\{\big[T^1_q(\underline{J})\ T^1_q(\underline{J})\big]\big[T^1(\underline{J}-\underline{L}-\underline{S}).\ T^1(\underline{J}-\underline{L}-\underline{S})\big]$$

$$+ \big[T^1(\underline{J}-\underline{L}-\underline{S}).\ T^1(\underline{J}-\underline{L}-\underline{S})\big]\big[T^1_q(\underline{J})\ T^1_q(\underline{J})\big]\Big\} \qquad (5.50)$$

An examination of the matrix elements of this operator (which will be given subsequently) shows that this is a new term to be included in the effective Hamiltonian (since there are no terms already present in the Hamiltonian with the same dependence on quantum numbers).

A similar treatment for the Λ-doubling term involving $\underline{p + 2q}$ reveals that a term of the form

$$H_{D_p} = -\tfrac{1}{2}D_p \sum_q{}^{\dagger} (-1)^q \Big\{\big[T^1_q(\underline{J})\ T^1_q(\underline{S})\big]\big[T^1(\underline{J}-\underline{L}-\underline{S}).\ T^1(\underline{J}-\underline{L}-\underline{S})\big]$$

$$+ \big[T^1(\underline{J}-\underline{L}-\underline{S}).\ T^1(\underline{J}-\underline{L}-\underline{S})\big]\big[T^1_q(\underline{J})\ T^1_q(\underline{S})\big]\Big\} \qquad (5.51)$$

has also to be included. D_p in this expression is defined as

$$D_p = -\sum_{v''\neq v} \frac{\langle v|\underline{p + 2q}|v''\rangle \langle v''|B|v\rangle}{E^0_v - E^0_{v''}} \qquad (5.52)$$

The Hamiltonian (5.51) is defined with a - sign so as to be consistent with the Hamiltonian (5.34).

The matrix elements of these two operators are rather complex but since these centrifugal distortion corrections have not been formulated in this form before they will, however, be quoted here.

① Matrix elements of D_q:

i) Contribution involving diagonal elements ($q' = 0$) of H_{ROT}.

$$\langle {}^2\Pi\Lambda=\pm1\ S\Sigma J\Omega M|H_{D_q}(q'=0)|{}^2\Pi\Lambda=\mp1\ S\Sigma'J'\Omega'M'\rangle$$

$$= D_q \sum_q{}^{\dagger} (-1)^q\, (-1)^{J-\Omega+J-\Omega''}\, J(J+1)(2J+1) \begin{pmatrix} J & 1 & J \\ -\Omega & q & \Omega'' \end{pmatrix} \begin{pmatrix} J & 1 & J \\ -\Omega'' & q & \Omega' \end{pmatrix}$$

$$\times \tfrac{1}{2}\big[2J(J+1) + 2S(S+1) - \Omega^2 - (\Omega')^2 - 2\Sigma^2\big]\ \delta_{\Sigma\Sigma'}$$

(5.53)

From $\Omega' = \Omega'' - q = \Omega - 2q$ we see that this term is a contribution to the matrix elements $\langle \Omega = \pm 3/2 | H | \Omega = \mp 1/2 \rangle$.

ii) Contributions involving off-diagonal elements ($q' = \pm 1$) of H_{ROT}. Only those terms which do not mix in other electronic states have to be considered, namely $-2B \sum_{q'}^{\dagger} T^{1}_{q'}(\underline{J})\, T^{1}_{-q'}(\underline{S})$. Two different contributions arise, one with $q' = -q$ and the other with $q' = +q$.

a) Term with $q' = -q$

$$\langle {}^{2}\Pi\ \Lambda = \pm 1\ S \Sigma J \Omega M | H_{D_q}(q' = -q) | {}^{2}\Pi\ \Lambda = \mp 1\ S \Sigma' J' \Omega' M' \rangle$$

$$= -D_q \sum_{q}^{\dagger} (-1)^{J-\Omega+S-\Sigma} \left[J(J+1)(2J+1)\right]^{\frac{1}{2}} \left[S(S+1)(2S+1)\right]^{\frac{1}{2}}$$

$$\times \begin{pmatrix} S & 1 & S \\ -\Sigma & -q & \Sigma' \end{pmatrix} \begin{pmatrix} J & 1 & J \\ -\Omega & q & \Omega' \end{pmatrix} \left[\begin{pmatrix} J & 1 & J \\ -\Omega & -q & \Omega'' \end{pmatrix}^{2} + \begin{pmatrix} J & 1 & J \\ -\Omega' & q & \Omega^{*} \end{pmatrix}^{2} \right] \qquad (5.54)$$

This matrix element connects states with $\Delta\Sigma = \pm 1$ and $\Delta\Omega = \mp 1$ and hence is of the form $\langle \Omega = \pm\frac{1}{2} | H | \Omega = \mp\frac{1}{2} \rangle$.

b) Term with $q' = +q$

$$\langle {}^{2}\Pi\ \Lambda = \pm 1\ S \Sigma J \Omega M | H_{D_q}(q' = q) | {}^{2}\Pi\ \Lambda = \mp 1\ S \Sigma' J' \Omega' M' \rangle$$

$$= 2D_q \sum_{q}^{\dagger} \left[J(J+1)(2J+1)\right]^{3/2} \left[S(S+1)(2S+1)\right]^{\frac{1}{2}} (-1)^{J-\Omega+S-\Sigma} (-1)^{q}$$

$$\times \begin{pmatrix} J & 1 & J \\ -\Omega & q & \Omega'' \end{pmatrix} \begin{pmatrix} J & 1 & J \\ -\Omega'' & q & \Omega^{*} \end{pmatrix} \begin{pmatrix} J & 1 & J \\ -\Omega^{*} & q & \Omega' \end{pmatrix} \begin{pmatrix} S & 1 & S \\ -\Sigma & q & \Sigma' \end{pmatrix} \qquad (5.55)$$

This is a contribution to $\langle \Omega = \pm 3/2 | H | \Omega = \mp 3/2 \rangle$ since $\Delta\Omega = \pm 3$ $\Delta\Sigma = \pm 1$.

② Matrix elements of D_p:

i) Contribution involving $q' = 0$ elements of H_{ROT}.

$$\langle {}^{2}\Pi\ \Lambda = \pm 1\ S \Sigma J \Omega M | H_{D_p}(q' = 0) | {}^{2}\Pi\ \Lambda = \mp 1\ S \Sigma' J' \Omega' M' \rangle$$

$$= \tfrac{1}{2} D_p \sum_{q}^{\dagger} (-1)^{q} (-1)^{J-\Omega+S-\Sigma} \left[S(S+1)(2S+1)\right]^{\frac{1}{2}} \left[J(J+1)(2J+1)\right]^{\frac{1}{2}}$$

$$\times \begin{pmatrix} J & 1 & J \\ -\Omega & q & \Omega' \end{pmatrix} \begin{pmatrix} S & 1 & S \\ -\Sigma & -q & \Sigma' \end{pmatrix} \left[2J(J+1) + 2S(S+1) - \Omega^{2} - \Sigma^{2} - (\Omega')^{2} - (\Sigma')^{2}\right]$$

$$(5.56)$$

This connects states with $\Delta\Omega = \pm 1$, $\Delta\Sigma = \mp 1$ and so is a contribution to $\langle \Omega = \pm\frac{1}{2} | H | \Omega = \mp\frac{1}{2} \rangle$.

ii) Contribution involving $q' = \pm 1$ elements of H_{ROT}. $q' = -q$ contributions are not present since these would have $\Delta\Sigma = \pm 2$ which is impermissible for doublet states.

The $q' = +q$ contribution is

$$\langle {}^2\Pi\ \Lambda = \pm 1\ S\Sigma J\Omega M | H_{D_p}(q' = \pm 1) | {}^2\Pi\ \Lambda = \mp 1\ S\Sigma' J'\Omega' M' \rangle$$

$$= D_p \sum_q{}^{\dagger} S(S+1)(2S+1)\ J(J+1)(2J+1) \begin{pmatrix} J & 1 & J \\ -\Omega & q & \Sigma'' \end{pmatrix} \begin{pmatrix} J & 1 & J \\ -\Omega'' & q & \Omega' \end{pmatrix}$$

$$\times \left[\begin{pmatrix} S & 1 & S \\ -\Sigma & q & \Sigma'' \end{pmatrix}^2 + \begin{pmatrix} S & 1 & S \\ -\Sigma & -q & \Sigma'' \end{pmatrix}^2 \right] \delta_{\Sigma\Sigma'} \qquad (5.57)$$

This gives a contribution to $\langle \Omega = \pm 3/2 | H | \Omega = \mp\frac{1}{2} \rangle$ since it connects states with $\Delta\Sigma = 0$, $\Delta\Omega = \pm 2$. All of the matrix elements (5.53) to (5.57) are diagonal in both J and M.

Third Order Hyperfine Interactions

These interactions arise from the admixture of vibrational or electronic states into the vibronic state $X^2\Pi(v = 0)$ as a result of off-diagonal elements in the hyperfine Hamiltonian. The operator form of these terms can be derived by a perturbation treatment, as was used for the centrifugal distortion terms already discussed. The usual hyperfine Hamiltonian (5.38) is of similar magnitude to terms arising from a second order treatment of the rotational Hamiltonian, and so we shall refer to it as a λ^2 Hamiltonian. A second order perturbation treatment of $\lambda^2 H_{hfs}$ leads to third order rotational terms - these are the third order (λ^3) hyperfine terms referred to in the heading above.

Both electronic and vibrational contributions to $\lambda^3 H_{hfs}$ arise just as for the centrifugal distortion terms. Consider first of all the electronic contributions - these arise from the second order perturbation terms containing matrix elements of the rotational and hyperfine Hamiltonians between electronic states:

$$\sum_{\eta''\Lambda''S''} \sum_{\gamma''} \frac{\langle {}^2\Pi; \gamma | H_{hfs} | \eta''\Lambda''S''\gamma'' \rangle \langle \eta''\Lambda''S''\gamma'' | H_{ROT} | {}^2\Pi; \gamma' \rangle}{(E^0_{{}^2\Pi} - E^0_{\eta''\Lambda''S''})} \qquad (5.58)$$

where γ refers to rotational, electron spin and nuclear spin wavefunctions. As before, the electronic wavefunctions can be factored off to give effective hyperfine constants of the form

$$\sum_{\eta''\Lambda''S''} \frac{\langle {}^2\Pi|(\lambda^2 \text{ hyperfine constant})|\eta''\Lambda''S''\rangle\langle\eta''\Lambda''S''|B|{}^2\Pi\rangle}{(E^0_{{}^2\Pi} - E^0_{\eta''\Lambda''S''})} \qquad (5.59)$$

B and the λ^2 hyperfine constants are functions of internuclear separation and so these λ^3 constants are in general non-zero. Only terms in the λ^2 hyperfine and rotational Hamiltonians that have matrix elements off-diagonal in electronic state need be considered. From (5.38), the only terms in $\lambda^2 H_{hfs}$ that can mix electronic states are the orbital hyperfine and nuclear spin/electron spin dipolar interactions:

$$a \sum_{q=\pm 1}^{\dagger} (-1)^q\, T^1_q(\underline{I})\, T^1_{-q}(\underline{L})$$

$$\beta' \sum_{q=\pm 1}^{\dagger} (-1)^q\, T^2_q(\underline{I}, \underline{S}) \qquad (5.60)$$

Note that β' is not the same as the β'' defined in (5.39) since the latter refers to the q = 0 component of $C^2_q(\Theta, \phi)$ whereas β' involves a $C^2_{\pm 1}(\Theta, \phi)$ factor. The only terms from the rotational Hamiltonian that have to be considered are the L-uncoupling and spin uncoupling terms

$$-2B \sum_q^{\dagger} T^1_q(\underline{J} - \underline{S})\, T^1_{-q}(\underline{L}) \qquad (5.61)$$

A second order perturbation treatment leads to four possible combinations of (5.60) and (5.61), as follows:

$$\sum_{\eta''\Lambda''S''} \sum_{\gamma''} (E^0_{{}^2\Pi} - E^0_{\eta''\Lambda''S''})^{-1}$$

$$\times \langle {}^2\Pi; \gamma | \sum_q^{\dagger} (-1)^q\, aT^1_q(\underline{I})\, T^1_{-q}(\underline{L})|\eta''\Lambda''S''\gamma''\rangle$$

$$\times \langle\eta''\Lambda''S''\gamma''| - 2B \sum_q^{\dagger} T^1_{\mp q}(\underline{J} - \underline{S})\, T^1_{\pm q}(\underline{L})|{}^2\Pi; \gamma'\rangle \qquad (5.62)$$

and

$$\sum_{\eta''\Lambda''S''} \sum_{\gamma''} (E^0_{^2\pi} - E^0_{\eta''\Lambda''S''})^{-1}$$

$$\times \langle {}^2\Pi ; \gamma | \sum_q{}^{\dagger} \beta' \, T^2_q(\underline{I}, \underline{S}) | \eta''\Lambda''S''\gamma'' \rangle$$

$$\times \langle \eta''\Lambda''S''\gamma'' | - 2B \sum_q{}^{\dagger} T^1_{\mp q}(\underline{J} - \underline{S}) \, T^1_{\pm q}(\underline{L}) | {}^2\Pi ; \gamma' \rangle \qquad (5.63)$$

Consider first of all the matrix elements from (5.62) and (5.63) involving the upper set of q components. The electronic wavefunctions can be factored off to give, respectively:

$$\sum_q{}^{\dagger} (-1)^q \left\{ \sum_{\eta''\Lambda''S''} \frac{\langle {}^2\Pi | a \, T^1_{-q}(\underline{L}) | \eta''\Lambda''S'' \rangle \langle \eta''\Lambda''S'' | - 2BT^1_q(\underline{L}) | {}^2\Pi \rangle}{(E^0_{^2\pi} - E^0_{\eta''\Lambda''S''})} \right\}$$

$$\times \langle \gamma | T^1_q(\underline{I}) | \gamma'' \rangle \langle \gamma'' | T^1_{-q}(\underline{J} - \underline{S}) | \gamma' \rangle \qquad (5.64)$$

and

$$\sum_q{}^{\dagger} (-1)^q \left\{ \sum_{\eta''\Lambda''S''} \frac{\langle {}^2\Pi | \beta' | \eta''\Lambda''S'' \rangle \langle \eta''\Lambda''S'' | - 2BT^1_q(\underline{L}) | {}^2\Pi \rangle}{(E^0_{^2\pi} - E^0_{\eta''\Lambda''S''})} \right\}$$

$$\times \langle \gamma | T^2_q(\underline{I}, \underline{S}) | \gamma'' \rangle \langle \gamma'' | T^1_{-q}(\underline{J} - \underline{S}) | \gamma' \rangle \qquad (5.65)$$

Equations (5.64) and (5.65) are just the matrix elements of the third order effective Hamiltonians

$$c_I \sum_q{}^{\dagger} (-1)^q \, T^1_q(\underline{I}) \, T^1_{-q}(\underline{J} - \underline{S}) \qquad (5.66)$$

and

$$D_{\beta'} \sum_q{}^{\dagger} (-1)^q \, T^2_q(\underline{I}, \underline{S}) \, T^1_{-q}(\underline{J} - \underline{S}) \qquad (5.67)$$

respectively, where

$$c_I = \sum_{\eta''\Lambda''S''} \frac{\langle {}^2\Pi | a \, T^1_{-q}(\underline{L}) | \eta''\Lambda''S'' \rangle \langle \eta''\Lambda''S'' | - 2BT^1_q(\underline{L}) | {}^2\Pi \rangle}{(E^0_{^2\pi} - E^0_{\eta''\Lambda''S''})}$$

$$(5.68)$$

$$D_{\beta'} = \sum_{\eta''\Lambda''S''} \frac{\langle {}^2\Pi|\beta'(-q)|\eta''\Lambda''S''\rangle\langle\eta''\Lambda''S''| - 2BT^1_q(\underline{L})|{}^2\Pi\rangle}{(E^0_{^2\Pi} - E^0_{\eta''\Lambda''S''})} \qquad (5.69)$$

The Hamiltonian (5.66) represents an effective nuclear-spin rotation interaction, the parameter for which is usually labelled C_I. We use the same symbol to conform to tradition. The symbol $D_{\beta'}$ is used by analogy with D_B, D_p, D_q etc. The Hamiltonian (5.67) describes the interaction of the rotational angular momentum with the tensor product of the electron and nuclear spins.

Both the $T^1_{\pm1}(\underline{L})$ and the $C^2_{\pm1}(\theta, \phi)$ operators shift the value of Λ by ∓1 and so, as for the Λ-doubling terms derived earlier, the excited states responsible for these third order terms are Σ or Δ states only. As before, matrix elements of (5.66) and (5.67) are diagonal in Λ.

If we treat the matrix elements of (5.62) and (5.63) involving the lower set of q components in a similar manner, two further hyperfine terms can be derived:

$$d_a \sum_q{}^{\dagger} (-1)^q\, T^1_q(\underline{I})\, T^1_q(\underline{J} - \underline{S}) \qquad (5.70)$$

and

$$d_{\beta'} \sum_q{}^{\dagger} (-1)^q\, T^2_q(\underline{I}, \underline{S})\, T^1_q(\underline{J} - \underline{S}) \qquad (5.71)$$

where

$$d_a = \sum_{\eta''\Lambda''S''} \frac{\langle {}^2\Pi|a\, T^1_{-q}(\underline{L})|\eta''\Lambda''S''\rangle\langle\eta''\Lambda''S''| - 2BT^1_{-q}(\underline{L})|{}^2\Pi\rangle}{(E^0_{^2\Pi} - E^0_{\eta''\Lambda''S''})} \qquad (5.72)$$

and

$$d_{\beta'} = \sum_{\eta''\Lambda''S''} \frac{\langle {}^2\Pi|\beta'(-q)|\eta''\Lambda''S''\rangle\langle\eta''\Lambda''S''| - 2BT^1_{-q}(\underline{L})|{}^2\Pi\rangle}{(E^0_{^2\Pi} - E^0_{\eta''\Lambda''S''})} \qquad (5.73)$$

The subscripts of these effective parameters indicate the λ^2 hyperfine term responsible. Small 'd's are used partly to distinguish them from $D_{\beta'}$ etc. and partly so as to be a similar notation to the λ^2 hyperfine Λ-doubling parameter, d, since examination of the electronic matrix elements reveals that these third order terms are also Λ-doubling hyperfine interactions. As for the ordinary Λ-doubling terms, the only excited states that contribute are $\sum$ states.

The complete third order hyperfine Hamiltonian arising from mixing of electronic states is the sum of equations (5.66), (5.67), (5.70) and (5.71). We note at this stage that since $T^2(\underline{I}, \underline{S})$ and $T^1(\underline{J} - \underline{S})$ do not commute it is necessary to take a Hermitian average of the terms involving $D_{\beta'}$ and $d_{\beta'}$. It was also necessary to take a Hermitian average of the term in d_a, since in the form given in (5.70) its matrix elements are non-Hermitian. The matrix elements of the four third order operators can be obtained using standard spherical tensor techniques and are as follows. In each case the $T^1(\underline{J})$ and $-T^1(\underline{S})$ terms from $T^1(\underline{J} - \underline{S})$ are considered separately. We use a decoupled basis set $|\Lambda S \Sigma J \Omega m_J\rangle |I m_I\rangle$ for these calculations.

① Matrix elements of C_I:

a) $T^1(\underline{J})$ part

$$\langle I m_I | \langle \Lambda S \Sigma J \Omega m_J | H_{C_I} | \Lambda S \Sigma' J' \Omega' m_J' \rangle | I m_I' \rangle$$

$$= C_I \sum_p (-1)^p (-1)^{I-m_I+J-m_J} \begin{pmatrix} I & 1 & I \\ -m_I & p & m_I' \end{pmatrix} [I(I+1)(2I+1)]^{\frac{1}{2}}$$

$$\times \begin{pmatrix} J & 1 & J \\ -m_J & -p & m_J' \end{pmatrix} [J(J+1)(2J+1)]^{\frac{1}{2}} \qquad (5.74)$$

These matrix elements are diagonal in J, Ω and Σ.

b) $T^1(\underline{S})$ part

Since $T^1(\underline{I}).T^1(\underline{S})$ is the form of the Fermi Contact interaction, this third order term is a contribution to α'.

② Matrix elements of $D_{\beta'}$:

a) $T^1(\underline{J})$ part

$$\langle I m_I | \langle \Lambda S \Sigma J \Omega m_J | H^{(J)}_{D_{\beta'}} | \Lambda S \Sigma' J' \Omega' m_J' \rangle | I m_I' \rangle$$

$$= D_{\beta'} \sum_q{}^{\dagger} \sum_{p,\, m} (-1)^{p+q} \sqrt{5} \begin{pmatrix} 1 & 1 & 2 \\ -m & m-q & q \end{pmatrix} (-1)^{J-\Omega+J-m_J+I-m_I+S-\Sigma}$$

$$\times \begin{pmatrix} I & 1 & I \\ -m_I & p & m_I' \end{pmatrix} [I(I+1)(2I+1)]^{\frac{1}{2}} \begin{pmatrix} S & 1 & S \\ -\Sigma & q-m & \Sigma' \end{pmatrix} [S(S+1)(2S+1)]^{\frac{1}{2}}$$

$$\times \begin{pmatrix} J & 1 & J' \\ -m_J & -p & m_J' \end{pmatrix} [(2J+1)(2J'+1)]^{\frac{1}{2}} \times \tfrac{1}{2} \Big\{ (-1)^{J'-\Omega} [J'(J'+1)(2J'+1)]^{\frac{1}{2}}$$

$$\times \begin{pmatrix} J & 1 & J' \\ -\Omega & -m & \Omega'' \end{pmatrix} \begin{pmatrix} J' & 1 & J' \\ -\Omega'' & q & \Omega' \end{pmatrix} + (-1)^{J-\Omega} [J(J+1)(2J+1)]^{\frac{1}{2}}$$

$$\times \begin{pmatrix} J & 1 & J \\ -\Omega & -q & \Omega'' \end{pmatrix} \begin{pmatrix} J & 1 & J' \\ -\Omega'' & m & \Omega' \end{pmatrix} \Bigg\} \tag{5.75}$$

m is a molecule fixed component of a first rank tensor, and can thus take the values m = 0, ±1. m = 0 gives a contribution to $\langle \pm 3/2 |\, | \pm 1/2 \rangle$ elements. m = ±1 gives elements diagonal in Ω.

b) $T^1(\underline{S})$ part

$$\langle I m_I | \langle \Lambda S \Sigma J \Omega m_J | H^{(S)}_{D_{\beta'}} | \Lambda S \Sigma' J' \Omega' m_J' \rangle | I m_I' \rangle$$

$$= D_{\beta'} \sum_q{}^{\dagger} \sum_{p,\, m} (-1)^{p+q} \sqrt{5} \begin{pmatrix} 1 & 1 & 2 \\ -m & m-q & q \end{pmatrix} (-1)^{J-\Omega+J-m_J+I-m_I}$$

$$\times \begin{pmatrix} I & 1 & I \\ -m_I & p & m_I' \end{pmatrix} \left[I(I+1)(2I+1)\right]^{\frac{1}{2}} \begin{pmatrix} J & 1 & J' \\ -\Omega & -m & \Omega' \end{pmatrix} \begin{pmatrix} J & 1 & J' \\ -m_J & -p & m_J' \end{pmatrix}$$

$$\times \left[(2J+1)(2J'+1)\right]^{\frac{1}{2}} \quad S(S+1)(2S+1) \begin{pmatrix} S & 1 & S \\ -\Sigma & q-m & \Sigma'' \end{pmatrix} \begin{pmatrix} S & 1 & S \\ -\Sigma'' & -q & \Sigma' \end{pmatrix} \tag{5.76}$$

m = 0 gives contributions diagonal in Ω

m = ±1 gives contributions to $\langle \pm 3/2 |\, | \pm 1/2 \rangle$ elements.

③ Matrix elements of d_a:

a) $T^1(\underline{J})$ part

$$\langle I m_I | \langle \Lambda S \Sigma J \Omega m_J | H_{d_a} | \Lambda \mp 2\ S \Sigma' J' \Omega' m_J' \rangle | I m_I' \rangle$$

$$= d_a \sum_q{}^{\dagger} \sum_p (-1)^{p+q} (-1)^{J-\Omega+J-m_J+I-m_I} \begin{pmatrix} I & 1 & I \\ -m_I & p & m_I' \end{pmatrix}$$

$$\times \left[I(I+1)(2I+1)\right]^{\frac{1}{2}} \begin{pmatrix} J & 1 & J' \\ -m_J & -p & m_J' \end{pmatrix} \left[(2J+1)(2J'+1)\right]^{\frac{1}{2}}$$

$$\times \tfrac{1}{2} \Bigg\{ (-1)^{J'-\Omega} \left[J'(J'+1)(2J'+1)\right]^{\frac{1}{2}} \begin{pmatrix} J & 1 & J' \\ -\Omega & -q & \Omega'' \end{pmatrix} \begin{pmatrix} J' & 1 & J' \\ -\Omega'' & -q & \Omega' \end{pmatrix}$$

$$+ (-1)^{J-\Omega} \left[J(J+1)(2J+1)\right]^{\frac{1}{2}} \begin{pmatrix} J & 1 & J \\ -\Omega & -q & \Omega'' \end{pmatrix} \begin{pmatrix} J & 1 & J' \\ -\Omega'' & -q & \Omega' \end{pmatrix} \Bigg\} \tag{5.77}$$

These give contributions to $\langle \pm 3/2 |\, | \mp 1/2 \rangle$ elements.

b) $T^1(\underline{S})$ part

$T^1_q(\underline{I})\ T^1_q(\underline{S})$ is the same form as the 'second order' Λ-doubling hyperfine interaction and hence this gives a contribution to d.

④ Matrix elements of $d_{\beta'}$:

a) $T^1(\underline{J})$ part

$$\langle Im_I|\langle \Lambda\, S\, \Sigma\, J\, \Omega\, m_J|H^{(J)}_{d_{\beta'}}|\Lambda \mp 2\ S\ \Sigma' J'\ \Omega' m'_J\rangle\,|Im'_I\rangle$$

$$= d_{\beta'} \sum_q{}^{\dagger} \sum_{p,\,m} (-1)^{p+q}\sqrt{5}\begin{pmatrix} 1 & 1 & 2 \\ -m & m-q & q \end{pmatrix}(-1)^{J-\Omega+J-m_J+S-\Sigma+I-m_I}$$

$$\times\begin{pmatrix} I & 1 & I \\ -m_I & p & m'_I \end{pmatrix}\left[I(I+1)(2I+1)\right]^{\frac{1}{2}}\begin{pmatrix} J & 1 & J' \\ -m_J & -p & m'_J \end{pmatrix}\left[(2J+1)(2J'+1)\right]^{\frac{1}{2}}$$

$$\times\begin{pmatrix} S & 1 & S \\ -\Sigma & q-m & \Sigma' \end{pmatrix}\left[S(S+1)(2S+1)\right]^{\frac{1}{2}} \times \tfrac{1}{2}\Big\{(-1)^{J'-\Omega}\left[J'(J'+1)(2J'+1)\right]^{\frac{1}{2}}$$

$$\times\begin{pmatrix} J & 1 & J' \\ -\Omega & -m & \Omega'' \end{pmatrix}\begin{pmatrix} J' & 1 & J' \\ -\Omega'' & -q & \Omega' \end{pmatrix} + (-1)^{J-\Omega}\left[J(J+1)(2J+1)\right]^{\frac{1}{2}}$$

$$\times\begin{pmatrix} J & 1 & J \\ -\Omega & -q & \Omega'' \end{pmatrix}\begin{pmatrix} J & 1 & J' \\ -\Omega'' & -m & \Omega' \end{pmatrix}\Big\} \qquad (5.78)$$

m = 0 elements give contributions to $\langle \pm 1/2|\ |\mp 1/2\rangle$

m = $\pm$1 elements contribute to $\langle \pm 3/2|\ |\mp 1/2\rangle$

b) $T^1(\underline{S})$ part

$$\langle Im_I|\langle \Lambda\, S\, \Sigma\, J\, \Omega\, m_J|H^{(S)}_{d_{\beta'}}|\Lambda \mp 2\ S\ \Sigma' J'\ \Omega' m'_J\rangle\,|Im'_I\rangle$$

$$= d_{\beta'} \sum_q \sum_{p,\,m} (-1)^{p+q}\sqrt{5}\begin{pmatrix} 1 & 1 & 2 \\ -m & m-q & q \end{pmatrix}(-1)^{J-\Omega+J-m_J+I-m_I}$$

$$\times\begin{pmatrix} I & 1 & I \\ -m_I & p & m'_I \end{pmatrix}\left[I(I+1)(2I+1)\right]^{\frac{1}{2}}\begin{pmatrix} J & 1 & J' \\ -m_J & -p & m'_J \end{pmatrix}\left[(2J+1)(2J'+1)\right]^{\frac{1}{2}}$$

$$\times\begin{pmatrix} J & 1 & J' \\ -\Omega & -m & \Omega' \end{pmatrix} S(S+1)(2S+1)\begin{pmatrix} S & 1 & S \\ -\Sigma & q-m & \Sigma'' \end{pmatrix}\begin{pmatrix} S & 1 & S \\ -\Sigma'' & q & \Sigma' \end{pmatrix} \qquad (5.79)$$

m = $\pm$1 matrix elements are of the same form as those of d, therefore this is a further contribution to d. m = 0 matrix elements are zero for doublet states since the sum rules on the 3-j symbols require $\Delta\Sigma = \pm 2$.

Note that the matrix elements $\langle \pm 3/2|H_{d_a}|\mp 1/2\rangle$ and $\langle \pm 3/2|H_{d_{\beta'}}|\mp 1/2\rangle$ differ only by a factor of Σ and certain numerical factors, and so these two terms are highly correlated. Only one of d_a and d_β, is determinable and so we shall suppress the d_a terms (since the remaining d_a terms can be included in d).

The vibrational contributions to the third order hyperfine Hamiltonian could be treated in a similar manner. In this case only terms in the λ^2 hyperfine Hamiltonian that are diagonal in electronic state have to be considered. The perturbation terms can be factorised to give effective parameters of the form

$$\sum_{v''\neq v} \frac{\langle v|(\lambda^2 \text{ hyperfine constant})|v''\rangle\langle v''|B|v\rangle}{(E_v^0 - E_{v''}^0)} \qquad (5.80)$$

However, since the magnitude of the hyperfine constants does not change drastically between vibrational levels (as is indicated by Clough _et al_ (16), where for J = 3/2 levels of OH the combined effects of a, α' and β'' change between vibrational states by about 3MHz and d changes by 0.1MHz - for higher rotational levels the changes are even more slight), the matrix elements $\langle v|(\lambda^2$ hfs constant$)|v''\rangle$ are expected to be very small. The vibrational contributions are likely to be far outweighed by the electronic contributions, and se we shall neglect them.

The complete hyperfine Hamiltonian to third order therefore consists of seven terms, only two of which cause Λ-doubling. Four of the hyperfine parameters can be related to the Frosch and Foley parameters and these are a, α', β'' and d, whereas the remaining three, C_I, D_β, and d_β, arise in third order of perturbation theory, and are therefore expected to be several orders of magnitude smaller.

5.6 Comparison with other Effective Hamiltonians

In this section we compare the form of the Hamiltonian derived in the preceding section with alternative formulations used by previous workers. All are similar in that a perturbation approach is adopted.

Consider first of all the rotational and fine-structure effective Hamiltonians, and in particular the Λ-doubling terms in this Hamiltonian. The earliest treatment of Λ-doubling in $^2\Pi$ electronic states was by Van Vleck (30) and these results were subsequently rederived in a form more useful for spectral analysis by Mulliken and Christy (21). We use the _q_ and _p + 2q_ Λ-doubling parameters introduced by the latter. Dousmanis, Sanders and Townes (7), henceforth referred to as DST, were the first to put an effective Λ-doubling Hamiltonian to any practical use, and we shall direct our interest to their Hamiltonian for the time being.

The DST Hamiltonian is of the form

$$H_{total} = H_{rfs} + H_{hfs} + H_{z} \qquad (5.81)$$

where H_{rfs} represents the rotational and spin-orbit Hamiltonians while H_{hfs} and H_{z} refer to hyperfine and Zeeman interactions. We shall ignore these latter two terms. Their Hamiltonian H_{rfs} is identical to our Hamiltonian (5.4). From H_{rfs}, DST derive an effective Hamiltonian operating only on $^2\Pi$ wavefunctions, by a perturbation treatment. The first order Hamiltonian is therefore just H_{rfs}, the matrix elements of which were given by Van Vleck (30). Apart from a difference in sign for the elements off-diagonal in Ω, these elements are identical to those obtained from our first order rotational/fine structure Hamiltonian H_{RSO}, given in (5.23). This sign difference arises simply because we have chosen a different phase convention to Van Vleck. Our phase convention is that of Condon and Shortley (31), under which the matrix elements

$$\langle \Omega | H_{ROT} | \Omega \pm 1 \rangle$$

are <u>negative</u>.

A second order calculation of the energy levels was performed by DST, leading to expressions for the energies of levels with a given J of the form

$$E = E_1 \pm E_2 \qquad (5.82)$$

where E_2 is the magnitude of the Λ-doubling splitting and E_1 gives the energies of the rotational levels in the absence of Λ-doubling. E_1 and E_2 are given by rather complex expressions involving both first and second order contributions and these are presented explicitly by DST. These expressions apply to a coupling scheme intermediate between Hund's cases a) and b). We are only interested in the Λ-doubling intervals, E_2. These are given by

$$E_2 = \nu^{(1)} + \nu^{(2)} \qquad (5.83)$$

where

$$\nu^{(1)} = -\alpha(J+\tfrac{1}{2})\left(\frac{\pm X + 2 - Y}{\pm X}\right) \mp \frac{4\beta}{X}(J-\tfrac{1}{2})(J+\tfrac{1}{2})(J+3/2) \qquad (5.84)$$

$\nu^{(2)}$ is given by a rather lengthy relationship, again involving α and β, and will not be quoted here. $\nu^{(2)}$ refers to higher order perturbation terms and is very much smaller than $\nu^{(1)}$. DST give $\nu^{(2)} \simeq \frac{1}{350}\nu^{(1)}$ for OH. The upper signs in (5.84) refer to $|\Omega| = 3/2$ fine structure levels of regular states and $|\Omega| = 1/2$ levels of inverted states. The reverse applies for the lower signs. The symbols in (5.84) are defined as follows:

$$X = \left[4(J+\tfrac{1}{2})^2 + Y(Y-4)\right]^{\frac{1}{2}} \qquad (5.85)$$

$$Y = A/B, \text{ as defined in section (5.2)}$$

$$\alpha = 4\sum_{\Sigma\,\text{states}} (-1)^s \frac{\langle\Pi|AL_y+2BL_y|\Sigma\rangle\langle\Sigma|BL_y|\Pi\rangle}{E_\Sigma - E_\Pi} \qquad (5.86)$$

$$\beta = 4\sum_{\Sigma\,\text{states}} (-1)^s \frac{|\langle\Pi|BL_y|\Sigma\rangle|^2}{E_\Sigma - E_\Pi} \qquad (5.87)$$

where s is even for Σ^+ states and odd for Σ^- states. α and β are Λ-doubling parameters, and, as mentioned in the previous section, can be related to the $\underline{q}$ and $\underline{p + 2q}$ parameters:

$$\begin{aligned} \underline{p + 2q} &= -2\alpha \\ \underline{q} &= -2\beta \end{aligned} \qquad (5.88)$$

Subsequent workers have generally used the Λ-doubling Hamiltonian of DST, or at least a modification of it. We are thus able to obtain numerical values for q and p + 2q for OH from the various studies that have been published. This comparison is not of the greatest value since we are not able to obtain any estimates for our D_p and D_q parameters. However, expression (5.84) is a potentially useful relationship in that we can use it to check the eigenvalues of our Λ-doubling Hamiltonians (5.32) and (5.34).

The most accurate determinations of Λ-doubling transition frequencies in OH come from the work of Dymanus and his group (12, 13, 14). The precision of their measurements necessitates the use of a more accurate Λ-doubling Hamiltonian than that of DST. We therefore turn to examine their effective Hamiltonian. In their analysis of the OH hyperfine Λ-doubling data (14) Meerts and Dymanus have used a Hamiltonian which they developed earlier to account for the Λ-doubling in NO (29). This was derived using the degenerate perturbation theory of Freed (32), and includes fine structure and hyperfine terms up to third order, their perturbation terms arising solely from the admixture of electronic states, not vibrational states.

Their work is therefore the most suitable for comparison with our effective Hamiltonian, and should thus provide estimates for all our zero-field parameters, bearing in mind that our D_p and D_q parameters involve vibrational mixing whereas Meerts and Dymanus third order terms involve electronic mixing.

Their perturbation method is very similar to our own in principle and so need not be detailed here. However, Meerts and Dymanus (henceforth referred to as MD) do not cast their perturbation expressions into an operator equivalent form, they merely extract electronic matrix elements and calculate the remaining matrix elements explicitly. Terms with the same J dependence are then collected together. The effective parameters therefore consist of sums of electronic matrix elements, each parameter modifying a rotational factor with a different J dependence. Indeed, this description is perhaps the simplest definition of an effective molecular parameter, and so could equally well be applied to our own parameters. The difference between these two formulations is that their parameters refer to different algebraic dependences of J whereas ours refer to different interactions of angular momenta. Our parameters are thus linear combinations of the MD parameters, or vice versa. The derivation of an effective Hamiltonian in the manner proposed by MD is somewhat lengthy and several algebraic manipulations are required in order to reach the desired form. A further difficulty with their Hamiltonian arises from their choice of symbols for the effective parameters. In an attempt to standardise notation they have introduced a set of fine-structure parameters α_i (i = 1 to 11), which are comprised of first, second and third order contributions. For instance

α_1 = A + 2nd and 3rd order terms

α_2 = B + 2nd and 3rd order terms

α_3 = $(\underline{p + 2q})$, or α, + 3rd order terms

α_6 = B + 2nd and 3rd order terms

α_7 = $\underline{q}$, or β, + 3rd order terms

This departure from traditional symbolism serves only to confuse the issue. Their expressions for the α_i's are further complicated in that another notation has to be introduced to describe the various electronic matrix elements involved.

All this notwithstanding, we are still able to make a comparison with our effective Hamiltonian.

The Hamiltonian matrix of MD is set up using Wang combinations as basis functions

$$|\pm\rangle = \frac{1}{\sqrt{2}}\left\{|J\Omega\Sigma\Lambda\rangle \pm (-1)^{s}\,|J\ -\Omega\ -\Sigma\ -\Lambda\rangle\right\} \tag{5.89}$$

where s is even for all electronic states except Σ^{-} states, in which case it is odd. To make a valid comparison we therefore have to set up our Hamiltonian matrix using similar basis functions. The relevant matrix elements are calculated initially in a non-paritised basis set (i.e. for states of a given J ≥ 3/2 the matrix is 4 x 4). From (5.23), (5.32), (5.34), and equations (5.53) to (5.57) we obtain

$$\begin{aligned}
\langle J, \Omega = \pm 1/2|H_{RSO}|J, \Omega = \pm 1/2\rangle &= -\tfrac{1}{2}A + B(J+1/2)^{2} \\
\langle J, \Omega = \pm 3/2|H_{RSO}|J, \Omega = \pm 3/2\rangle &= \tfrac{1}{2}A + B\left[(J+1/2)^{2} - 2\right] \\
\langle J, \Omega = \pm 3/2|H_{RSO}|J, \Omega = \pm 1/2\rangle &= -B\left[(J-1/2)(J+3/2)\right]^{\frac{1}{2}} \\
\langle J, \Omega = \pm 3/2|H_{LD}(\underline{q})|J, \Omega = \mp 1/2\rangle &= -\tfrac{1}{2}\underline{q}(J+1/2)\left[(J-1/2)(J+3/2)\right]^{\frac{1}{2}} \\
\langle J, \Omega = \pm 1/2|H_{LD}(\underline{p+2q})|J, \Omega = \mp 1/2\rangle &= \tfrac{1}{2}\underline{(p+2q)}(J+1/2) \\
\langle J, \Omega = \pm 1/2|H_{D_p}|J, \Omega = \mp 1/2\rangle &= \tfrac{1}{2}D_{p}(J+1/2)^{3} \\
\langle J, \Omega = \pm 3/2|H_{D_p}|J, \Omega = \mp 1/2\rangle &= -\tfrac{1}{4}D_{p}(J+1/2)\left[(J-1/2)(J+3/2)\right]^{\frac{1}{2}} \\
\langle J, \Omega = \pm 3/2|H_{D_q}|J, \Omega = \mp 3/2\rangle &= \tfrac{1}{2}D_{q}(J-1/2)(J+1/2)(J+3/2) \\
\langle J, \Omega = \pm 1/2|H_{D_q}|J, \Omega = \mp 1/2\rangle &= \tfrac{1}{2}D_{q}(J-1/2)(J+1/2)(J+3/2) \\
\langle J, \Omega = \pm 3/2|H_{D_q}|J, \Omega = \mp 1/2\rangle &= -\tfrac{1}{2}D_{q}\left\{(J+1/2)^{3}-(J+1/2)\right\}\left[(J-1/2)(J+3/2)\right]^{\frac{1}{2}}
\end{aligned} \tag{5.90}$$

From these we construct a matrix in the Wang basis set, and this is given in Table 3. The corresponding matrix of MD is given in Table 4. Note that the matrix elements $\langle 3/2|H_{RSO}|1/2\rangle$ differ in sign - this is because we have used the opposite phase convention to MD, and this difference has to be allowed for when the other $\langle 3/2| \; |1/2\rangle$ elements are compared. A direct comparison of Tables 3 and 4, with allowances for differences in phase conventions, leads to the following set of relationships:

$$\begin{aligned} (2\alpha_3 - \alpha_5) &\equiv \tfrac{1}{2}\,(\underline{p + 2q}) - \tfrac{1}{2}D_q \\ (\alpha_4 + \alpha_5) &\equiv \tfrac{1}{2}\,(D_p + D_q) \\ \alpha_7 &\equiv \tfrac{1}{2}\,(\underline{q} + \tfrac{1}{2}D_p - Dq) \\ \alpha_8 &\equiv \tfrac{1}{2}D_q \end{aligned} \qquad (5.91)$$

Note that there are no terms unique to either Hamiltonian, from which we can conclude that the third order effects of vibrational mixing are of the same form, and therefore inseparable, from those of electronic mixing. Using these relations we are able to obtain values for $\underline{q}$, $\underline{p + 2q}$, D_p and D_q from Meerts and Dymanus's analysis of OH (14). Note that whereas MD have five Λ-doubling constants, we only have four. However, their term in α_5 can be rewritten as $\pm\alpha_5(J+1/2)^3 \mp \alpha_5(J+1/2)$, these two terms being of the same J dependence as α_4 and α_3 elements, respectively, and thus MD only have four independent parameters. Indeed, in their analyses of NO (29) and OH (14) MD were only able to determine four Λ-doubling constants. From an examination of the electronic matrix elements that constitute the third order parameters, the relationship

$$\alpha_5 = \frac{B_\pi}{B_\pi - B_\Sigma}\,\alpha_8 \qquad (5.92)$$

can be obtained. Thus either α_5 or α_8 could be suppressed. MD chose to suppress the α_8 parameter in their NO and OH studies. Since we require an α_8 value as a starting point in the estimation of our own parameters from (5.91) we therefore have to calculate it from α_5 using (5.92).

The existence of direct relationships between our effective Hamiltonian and that of MD gives some vindication of our approach. It is worth pointing out that the derivation of our Hamiltonian is straightforward and leads directly to an operator equivalent form whereas, by contrast, the MD deriv-

Table 3 Matrix elements of our fine structure Hamiltonian in a Wang basis.

	$\|3/2\rangle$	$\|1/2\rangle$
$\langle 3/2\|$	$A/2 + B[(J+1/2)^2 - 2]$ $\pm D_q(J-1/2)(J+1/2)(J+3/2) \times 1/2$	$-B[(J-1/2)(J+3/2)]^{1/2}$ $\mp \underline{q}(J+1/2)[(J-1/2)(J+3/2)]^{1/2} \times 1/2$ $\mp D_p(J+1/2)[(J-1/2)(J+3/2)]^{1/2} \times 1/4$ $\mp D_q(J+1/2)\{(J+1/2)^2 - 1\}[(J-1/2)(J+3/2)]^{1/2} \times 1/2$
$\langle 1/2\|$		$-A/2 + B(J+1/2)^2$ $\pm\underline{(p+2q)}(J+1/2) \times 1/2$ $\pm D_q(J-1/2)(J+1/2)(J+3/2) \times 1/2$ $\pm D_p(J+1/2)^3 \times 1/2$

Table 4 Fine structure matrix elements due to Meerts and Dymanus (29), in a Wang basis.

	$\|3/2\rangle$	$\|1/2\rangle$
$\langle 3/2\|$	$A/2 + B[J(J+1) - 7/4]$ $\pm \alpha_8 (J-1/2)(J+1/2)(J+3/2)$	$\alpha_6 [(J-1/2)(J+3/2)]^{1/2}$ $\pm \alpha_7 (J+1/2)[(J-1/2)(J+3/2)]^{1/2}$ $\pm \alpha_8 (J+1/2)^3 [(J-1/2)(J+3/2)]^{1/2}$
$\langle 1/2\|$		$-\alpha_1/2 + \alpha_2 (J+1/2)^2$ $\pm 2\alpha_3 (J+1/2) \pm \alpha_4 (J+1/2)^3$ $\pm \alpha_5 (J-1/2)(J+1/2)(J+3/2)$

$\alpha_1 \simeq A$ $\qquad$ $\alpha_2 \simeq B$ $\qquad$ $\alpha_6 \simeq B$

ation is both long and messy. In addition we do not need to introduce any unnecessary nomenclature and are able to retain traditional symbols for effective parameters.

We now turn to the hyperfine Hamiltonian. Most workers have used the Frosch and Foley Hamiltonian (with minor corrections by Dousmanis (33)) and the relationship between this and our 'second-order' hyperfine Hamiltonian has already been given in the previous section. As regards the third order terms we again have to turn to the work of Meerts and Dymanus. Their paper on NO (29) contains a derivation of third order hyperfine terms, and some sort of correlation between this and our Hamiltonian is sought. However it is difficult to make a direct numerical comparison on two counts. First, they have calculated their matrix elements in a coupled basis whereas ours have been calculated in a decoupled basis. There is of course no reason why we should not calculate our elements in a coupled basis, for the purposes of comparison only. However, in view of the length of the calculations involved, the small size of third order parameters and the fact that we are (in principle) able to determine them ourselves from a least-squares analysis of available zero-field data, this would seem to be an example of the law of diminishing returns.

Secondly, MD have assumed that hyperfine matrix elements off-diagonal in J are negligibly small. These elements are likely to be very small in OH since the spacings between consecutive levels is so large, but they will be more important in NO. Since MD have data of very high precision from their molecular beam studies this assumption is not really justified in their case. In a recent paper, Meerts (34) has reanalysed the NO data with a Hamiltonian that does include these off-diagonal states and this greatly improved the quality of the fit. No reanalysis of the OH data has yet been published.

MD's hyperfine Hamiltonian is derived in a similar manner to their fine structure Hamiltonian, and suffers from the same drawbacks. Again, a new and confusing symbolism has been introduced - nine hyperfine constants, labelled χ_i ($i = 1$ to 9), which are linear combinations of twelve different β constants and a C_{RS} constant, the β terms representing various electronic matrix elements. If third-order effects are neglected, their parameters χ_1, χ_2, χ_3 and χ_4 can be related to the Frosch and Foley a, b, c and d constants and hence to our own a, α', β'' and d. The remaining χ parameters are comprised of third order terms only. One might inquire as to why MD have nine constants whereas we only have seven determinable parameters. The reason for this is that there is an error in their derivation -

the L-uncoupling operator has no matrix elements between Π states and yet MD have included them. If we set to zero all the terms involving such elements we find that their β_7, β_{10} and β_{11}, and consequently their χ_6 and χ_8 parameters, vanish. Thus to third order MD have only seven determinable parameters, and only two of these, χ_2 and χ_9, are Λ-doubling terms. This is consistent with our Hamiltonian, in which we found that only two Λ-doubling constants, d and either d_a or $d_{\beta'}$, are determinable. We expect the d and $d_{\beta'}$ constants to be linear combinations of χ_2 and χ_9. Contributions to elements $\langle 3/2|H_{hfs}|1/2\rangle$ arise only from χ_9 so we can infer that χ_9 is related in some simple manner to $d_{\beta'}$ only (since d has no such matrix elements).

A nuclear spin-rotation interaction has been included in the MD Hamiltonian operator, their parameter being labelled C_{RS}, after Freed (32). This is identical to our C_I. The value of C_{RS} is not determined directly in their analysis as it is absorbed into their χ parameters, but it is possible to get an estimate for it. After crossing out the L-uncoupling matrix elements mentioned above we find that

$$\beta_5 = -\beta_6 \tag{5.93}$$

$$\text{and} \quad \beta_8 \simeq \beta_9 \simeq 0 \tag{5.94}$$

β_8 and β_9 are approximately zero since they involve matrix elements between $X^2\Pi$ and excited Δ states. If there are any Δ states for OH the energy difference $(E^0_{2\pi} - E^0_{\Delta})$ is likely to be very large and so the perturbation corrections β_8 and β_9 will be very small. Substitution of the relations (5.93) and (5.94) into the expressions for the χ_5 and χ_7 parameters leads to

$$\chi_5 \simeq \beta_5 + C_{RS} \tag{5.95}$$

$$\chi_7 \simeq -\beta_5 + C_{RS} \tag{5.96}$$

$$\text{Thus} \quad C_I \equiv C_{RS} \simeq \tfrac{1}{2}(\chi_5 + \chi_7) \tag{5.97}$$

MD were not able to determine all nine of their hyperfine constants for OH - χ_8 was not found and only the combination $(\chi_5 + \chi_7)$ was determined, not χ_5 and χ_7 individually. This is ideal for a determination of C_{RS} but unfortunately renders impossible an evaluation of $D_{\beta'}$ from their results.

Terms in $D_{\beta'}$ appear in the elements $\langle 3/2|H|3/2\rangle$, $\langle 1/2|H|1/2\rangle$ and

$\langle 3/2|H|1/2\rangle$. Assuming only Σ states contribute, examination of the corresponding MD elements and the β contributions to their parameters reveals that χ_1, χ_4, χ_5 and χ_7 are likely to be correlated in some way with the $D_{\beta'}$ parameter. It is likely therefore that $D_{\beta'}$ corresponds to the β_5 (and β_6) contributions to χ_5 and χ_7. Since neither χ_5, χ_7 nor $(\chi_5 - \chi_7)$ have been determined, $D_{\beta'}$ cannot be determined from these parameters. It is not possible to construct a suitable set of simultaneous equations in β_5 by including χ_1 and χ_4 either. MD (14) state that the reason χ_5 and χ_7 cannot be found separately is because they are strongly correlated with the χ_4 constant and only two constants can be determined independently. They therefore chose to determine the two parameters χ_4 and $(\chi_5 + \chi_7)$, although in principle all three could be found. This unfortunately does not augur well for our proposed determination of $D_{\beta'}$ by least-squares fitting.

5.7 Molecular Zeeman Effect

We have dealt briefly with the Zeeman effect in section (5.2), and have explained its significance in e.p.r. studies. In this section we present the form of the Zeeman Hamiltonian used to describe the energies of the Zeeman levels, and we discuss in more detail the relationship between our g-factors and the phenomenological g-factors of Radford (4, 5).

The general Zeeman Hamiltonian is defined as

$$H_z = g_S \mu_B T^1(\underline{B}) \cdot T^1(\underline{S}) + g_L \mu_B T^1(\underline{B}) \cdot T^1(\underline{L})$$

$$- g_r \mu_B T^1(\underline{B}) \cdot T^1(\underline{J} - \underline{L} - \underline{S}) - g_N \mu_N T^1(\underline{B}) \cdot T^1(\underline{I}) \qquad (5.98)$$

where these terms describe the interaction of the magnetic field $\underline{B}$ with, respectively, the electron spin, electron orbital, nuclear rotation and nuclear spin angular momenta. This Hamiltonian is used as a starting point by Radford (4) also. In contrast to Radford, we define the interaction between $\underline{B}$ and $\underline{I}$ with a negative sign, since the magnetic moment of a particle is proportional to its charge and hence the magnetic moment of a nucleus will be of opposite sign to that of the electron. The term in g_r we also define to be negative - this term contains contributions from the rotation of the nuclei and from the electrons that rotate with the nuclei, and the former and expected to outweigh the latter.

The dominant contributions in (5.98) will be from the terms in g_S and g_L, and the values of these g-factors are expected to be close to their free electron values, given in (5.16) as $g_S = 2.00232$ and $g_L = 1.000$. The term in g_N is expected to be very small since the magnetic moment is proportional to μ_N rather than μ_B. g_N for a proton is $g_N = 5.585486$ but since $\mu_N/\mu_B \simeq 1/1850$ then the contribution from this term ($g_N\mu_N/\mu_B$) will be about 10^{-3} of that from the electronic g-factors. g_r will be smaller than $g_N\mu_N/\mu_B$ since it will involve a nuclear contribution, with some cancellation by electronic contributions. A value of about 10^{-4} is to be expected.

The Hamiltonian (5.98) contains terms that mix electronic states, namely the $q = \pm 1$ components of the terms in g_L and g_r, although the latter we can safely ignore because of their small size. An effective Hamiltonian is therefore derived that operates only on $^2\Pi$ wavefunctions and to first order this Hamiltonian is comprised of those terms in H_z that do not mix electronic states. The magnetic field vector is quantised in a space-fixed frame, and the space-fixed z axis is defined as the direction of the applied magnetic field. Thus from equation (2.31) we have

$$B_0 = T^1_{p=0}(\underline{B}) \qquad (5.99)$$

where B_0 is the applied magnetic flux density. The first-order effective Zeeman Hamiltonian can now be rewritten in terms of p = 0 components only:

$$\begin{aligned} H_z^{(1)} &= P_0 H_z P_0 \\ &= g_S\mu_B B_0 T^1_0(\underline{S}) + g_L\mu_B B_0 T^1_0(\underline{L}) \\ &\quad - g_r\mu_B B_0 T^1_0(\underline{J} - \underline{L} - \underline{S}) - g_N\mu_N B_0 T^1_0(\underline{I}) \qquad (5.100) \end{aligned}$$

The matrix elements of this operator can be easily calculated using standard spherical tensor techniques.

The effects of mixing in other electronic states can be included by going to higher orders in perturbation theory. The dominant second order contributions arise from cross terms of the $q = \pm 1$ terms in g_L with the L-uncoupling terms and terms uncoupling $\underline{S}$ from $\underline{L}$. These latter operators we have previously called V_1 and V_2 respectively (see equation (5.24)). We shall regroup these to give V_1' and V_2' as follows:

$$V_1' = -2B \sum_q{}^{\dagger} (-1)^q \, T^1_q(\underline{L}) \, T^1_{-q}(\underline{J} - \underline{S}) \qquad (5.101)$$

$$V_2' = A \sum_q^{\dagger} (-1)^q \, T^1_q(\underline{L}) \, T^1_{-q}(\underline{S}) \tag{5.102}$$

The relevant terms in g_L we shall call V_3:

$$V_3 = g_L \mu_B B_0 \sum_q^{\dagger} \mathcal{D}^{(1)}_{0q}(\omega)^* \, T^1_q(\underline{L}) \tag{5.103}$$

The second order effective Zeeman Hamiltonian is therefore of the form

$$\begin{aligned} H_z^{(2)} &= \lambda^2 P_0 V \, (Q_0/a) \, V P_0 \\ &= \sum_{\eta''\Lambda''S''\gamma''} \frac{\langle {}^2\Pi; \gamma | V_3 | \eta''\Lambda''S''\gamma'' \rangle \langle \eta''\Lambda''S''\gamma'' | V_1' + V_2' | {}^2\Pi; \gamma' \rangle}{E^0_{2\Pi} - E^0_{\eta''\Lambda''S''}} \end{aligned} \tag{5.104}$$

Consider the cross terms between V_2' and V_3:

$$\begin{aligned} H^{(2)}(V_2'V_3) &= \sum_{\eta''\Lambda''S''\gamma''} \left(E^0_{2\Pi} - E^0_{\eta''\Lambda''S''}\right)^{-1} \\ &\times \langle {}^2\Pi; \Lambda S \Sigma J \Omega M | g_L \mu_B B_0 \sum_q^{\dagger} \mathcal{D}^{(1)}_{0q}(\omega)^* \, T^1_q(\underline{L}) | \eta''\Lambda''S''\Sigma''J''\Omega''M'' \rangle \\ &\times \langle \eta''\Lambda''S''\Sigma''J''\Omega''M'' | A \sum_{q'}^{\dagger} (-1)^{q'} T^1_{q'}(\underline{L}) T^1_{-q'}(\underline{S}) | {}^2\Pi; \Lambda' S \Sigma' J' \Omega' M' \rangle \end{aligned} \tag{5.105}$$

where $q' = \pm q$. The electronic wavefunctions can be factored off to give

$$\begin{aligned} &\sum_{q,\,q'}^{\dagger} \Big\{ \left(E^0_{2\Pi} - E^0_{\eta''\Lambda''S''}\right)^{-1} \\ &\times \langle {}^2\Pi, \Lambda | g_L T^1_q(\underline{L}) | \eta''\Lambda''S'' \rangle \langle \eta''\Lambda''S'' | A(-1)^{q'} T^1_{q'}(\underline{L}) | {}^2\Pi, \Lambda' \rangle \Big\} \\ &\times \mu_B B_0 \langle J \Omega M | \mathcal{D}^{(1)}_{0q}(\omega)^* | J' \Omega' M' \rangle \langle S \Sigma | T^1_{-q'}(\underline{S}) | S \Sigma' \rangle \end{aligned} \tag{5.106}$$

where use has been made of the fact that $\underline{S}$ operates only on spin functions and $\mathcal{D}^{(1)}(\omega)^*$ only on rotational functions. The spin and rotational matrix elements in (5.106) are just the matrix elements of an operator of the form

$$\sum_q^{\dagger} \mathcal{D}^{(1)}_{0q}(\omega)^* \, T^1_{\pm q}(\underline{S}) \tag{5.107}$$

The terms in braces in (5.106) are effective parameters that can be identified as g-factors. We therefore define:

For q' = -q,

$$g_1 = \sum_{\substack{\eta''\Lambda''S'' \\ (q)}} \frac{\langle {}^2\Pi, \Lambda | g_L T^1_q(\underline{L}) | \eta''\Lambda''S'' \rangle \langle \eta''\Lambda''S'' | A(-1)^q \, T^1_{-q}(\underline{L}) | {}^2\Pi, \Lambda' \rangle}{(E^0_{2\Pi} - E^0_{\eta''\Lambda''S''})} \tag{5.108}$$

For q' = q,

$$g_1' = \sum_{\substack{\eta''\Lambda''S'' \\ (q)}} \frac{\langle {}^2\Pi, \Lambda | g_L T^1_q(\underline{L}) | \eta''\Lambda''S'' \rangle \langle \eta''\Lambda''S'' | A(-1)^q \, T^1_q(\underline{L}) | {}^2\Pi, \Lambda' \rangle}{(E^0_{2\Pi} - E^0_{\eta''\Lambda''S''})} \tag{5.109}$$

Hence equation (5.103) can be rewritten in an operator equivalent form

$$\begin{aligned} H^{(2)}(V_2' V_3) &= g_1 \mu_B B_0 \sum_q^{\dagger} \mathcal{D}^{(1)}_{0q}(\omega)^* \, T^1_q(\underline{S}) \\ &\quad + g_1' \mu_B B_0 \sum_q^{\dagger} \mathcal{D}^{(1)}_{0q}(\omega)^* T^1_{-q}(\underline{S}) \end{aligned} \tag{5.110}$$

Similarly the cross terms between V_1' and V_3 can be written as

$$\begin{aligned} H^{(2)}_{V_1' V_3} &= g^e_r \mu_B B_0 \sum_q^{\dagger} \mathcal{D}^{(1)}_{0q}(\omega)^* \, T^1_q(\underline{J} - \underline{S}) \\ &\quad + g^{e'}_r \mu_B B_0 \sum_q^{\dagger} \mathcal{D}^{(1)}_{0q}(\omega)^* \, T^1_{-q}(\underline{J} - \underline{S}) \end{aligned} \tag{5.111}$$

Here $$g^e_r = \sum_{\substack{\eta''\Lambda''S'' \\ (q)}} \frac{\langle {}^2\Pi, \Lambda | g_L T^1_q(\underline{L}) | \eta''\Lambda''S'' \rangle \langle \eta''\Lambda''S'' | -2B(-1)^q \, T^1_{-q}(\underline{L}) | {}^2\Pi, \Lambda' \rangle}{(E^0_{2\Pi} - E^0_{\eta''\Lambda''S''})} \tag{5.112}$$

$$\text{and} \quad g_r^{e'} = \sum_{\substack{\eta''\Lambda''S'' \\ (q)}} \frac{\langle {}^2\Pi, \Lambda \,|\, g_L T_q^1(\underline{L}) \,|\, \eta''\Lambda''S'' \rangle \langle \eta''\Lambda''S'' \,|\, -2B(-1)^q \, T_q^1(\underline{L}) \,|\, {}^2\Pi, \Lambda' \rangle}{(E^0_{{}^2\Pi} - E^0_{\eta''\Lambda''S''})} \tag{5.113}$$

The symbols for these second order g-factors have been chosen so as to be consistent with Carrington and Lucas (35) - the second order effective Hamiltonian and parameter definitions given above can also be found in their paper. The matrix elements of the second order Hamiltonian can be calculated without much difficulty - those of g_l' have already been quoted by Carrington and Lucas (35).

An examination of the electronic matrix elements in (5.108), (5.109), (5.112) and (5.113) reveals, just as for the Λ-doubling terms treated in section (5.5), that the terms with $q' = -q$ are overall diagonal in Λ whereas those with $q' = q$ have matrix elements between states differing in Λ by ± 2, i.e. are Λ-doubling terms. Hence g_l and g_r^e are non-Λ-doubling g-factors and contain contributions from both Σ and Δ states; g_l' and $g_r^{e'}$ are Λ-doubling g-factors containing contributions from Σ states only.

We now deal with the significance of these four second-order g-factors. The term in g_S in the first order Hamiltonian has $q = 0$ and ± 1 elements and hence describes an isotropic interaction. It conveys information on a spherical distribution of electronic charge. The g_l term has matrix elements similar to those of g_S except that it has only $q = \pm 1$ elements. This term therefore carries information on the deviations from spherical symmetry, and for this reason is known as the spin-anisotropy g-factor. We generally identify the $q = 0$ component as lying along the internuclear (z) axis and so g_l describes the electronic charge distribution perpendicular to the internuclear axis. g_l' is similar to g_l, except that it has matrix elements connecting Λ-doublets and will give information exclusively on the admixture of Σ states. The matrix elements of g_r^e and $g_r^{e'}$ are similar to those of g_r, except that there is no $T_0^1(\underline{L})$ contribution. Both represent anisotropic corrections to g_r arising from the rotation of the electrons with the nuclei. The g_r^e term is absorbed into g_r, and hence represents those electronic contributions to g_r that were mentioned previously.

It is interesting to compare our effective Zeeman operator with that of Radford (4), who also uses a perturbation approach. Radford reduces his results to a phenomenological form rather than cast them in an operator equivalent form, as we do. The dominant contribution to the Zeeman splitting arises from the linear Zeeman effect, which has the general form given in (5.14) and (5.15):

$$E_{Zeeman} = -m_z B_0 = -g_J \mu_B m_J B_0$$

where g_J is an effective g-factor for a particular rotational level, J. There are no matrix elements of the linear Zeeman operator connecting different rotational states. Radford (4) gives the phenomenological form of the linear Zeeman effect arising from the Hamiltonian (5.98) as

$$E_{z_1} = \mu_B B_0 \left[g_J^{\pm} m_J + g_I m_I \right] \qquad (5.114)$$

where $g_J^{\pm}$ are phenomenological molecular g-factors referring to rotational levels, J, of $\pm$ parity. g_I is a nuclear spin g-factor which is related to our g_N by $g_N = \frac{-\mu B}{\mu N} g_I$. These linear Zeeman energies correspond to the eignevalues of our Zeeman Hamiltonian with the restriction that only matrix elements diagonal in J are used.

In the presence of an external magnetic field J is not a good quantum number, so there are matrix elements between states of different J. A correction for these terms has to be applied to the linear Zeeman energies with the effect that the energy levels no longer tune linearly with field. In our case these corrections come from the off-diagonal J terms in our effective Hamiltonian, and are <u>linear</u> in magnetic field. This is known as the second order Zeeman effect. Radford, however, obtains his energies by an explicit perturbation calculation rather than by our method of computer diagonalisation of the complete Hamiltonian matrix. As a result these second order effects will manifest themselves as a power series in B_0, starting with quadratic terms. Expressions for the quadratic and cubic Zeeman energies are given by Radford as

$$E_{z_2} = (K_0 + K_2 m_J^2) \frac{(\mu_B B_0)^2}{hc} \qquad (5.115)$$

$$E_{z_3} = (K_1 m_J + K_3 m_J^3) \frac{(\mu_B B_0)^3}{(hc)^2} \qquad (5.116)$$

The K_i's are perturbation expressions, which Radford determines phenomenologically. A word is in order regarding these two expressions. Radford states that the K_i's are dimensionless constants, but if they are then the dimensions on each side of the equality signs do not balance. These equations require (hc) to be an energy, which is not correct. Consider the expression for E_{z_2} - the perturbation expression for this will be of the form

$$E_{z_2} = (g_J^{\pm})^2 \frac{|\langle J| \ |J'\rangle|^2}{hB[J'(J'+1) - J(J+1)]} (\mu_B B_0)^2 m_J^2 \qquad (5.117)$$

where B is the rotational constant, in H_z, and $J' = J + 1$. If instead B is chosen to be in cm^{-1} this expression becomes

$$E_{z_2} = \left\{ (g_J^{\pm})^2 \frac{|\langle J| \ |J+1\rangle|^2}{2B(J+1)} \right\} m_J^2 \frac{(\mu_B B_0)^2}{hc} \qquad (5.118)$$

which is then equivalent to Radford's expression. The term in braces can be identified with K_2 and can be seen to have dimensions of cm, contrary to Radford's statements.

The expressions of interest to use are the $g_J^{\pm}$ terms. Radford defines these to be

$$g_J^{\pm} = g_J^0 + (\delta g_J)_S + (\delta g_J)_N + (\delta g_J)_L^{\pm} \qquad (5.119)$$

g_J^0 contains contributions from g_S and g_L. $(\delta g_J)_S$ corrects for the anomolous part of the electron spin g-factor, i.e. the deviation in g_S from 2. $(\delta g_J)_N$ corrects for the rotation of the nuclei and hence can be correlated with our g_r. Finally, $(\delta g_J)_L^{\pm}$ refers to corrections arising from the rotation of the electrons with the nuclei and so should correspond to our g_r^e and $g_r^{e'}$. There seem to be no terms corresponding to our g_l and g_l'. The fundamental molecular g-factors proposed by us are of far more use than the effective g-factors of Radford. His measured $g_J^{\pm}$ values contain information on the contributions from the rotation of the nuclei and so on but, written in this form, this information is irretrievable. All that this approach allows is an ab initio calculation of these corrections to g_J^0 so that theoretical values of $g_J^{\pm}$ can be compared with the measured ones. Although Radford has been able to deduce much from making such comparisons it nevertheless makes more sense to determine the fundamental g-factors directly. Information on electron distributions and so on would then be much more readily available.

It is to be expected that Radford's $g_J^{\pm}$ parameters will be linear combinations of the more fundamental g-factors. It would be of interest to determine this relationship on more quantitative grounds. We shall therefore calculate the matrix elements of the linear Zeeman effect for the F_2

levels of OH, using both approaches, and ignoring nuclear spins. A similar calculation for the F_1 levels has already been performed (36). In the case b) limit F_1 and F_2 refer to states with $J = N + \frac{1}{2}$ and $J = N - \frac{1}{2}$ respectively. In the case a) limit these correlate with $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ levels respectively, for an inverted state. Hence we wish to calculate the linear Zeeman effect for the $^2\Pi_{1/2}$ state of OH. Using Radford's approach these energies are given immediately from (5.114):

$$E = (\bar{g}_J \pm \tfrac{1}{2}\Delta g_J)\,\mu_B B_0 m_J \qquad (5.120)$$

where $$\bar{g}_J = \tfrac{1}{2}(g_J^+ + g_J^-) \qquad (5.121)$$

and $$\Delta g_J = (g_J^+ - g_J^-) \qquad (5.122)$$

It is more difficult to obtain similar expressions using our approach since we have to allow for the effects of intermediate coupling. From DST (7) we find that the wavefunctions for F_1 levels are given by

$$|\pm;\, F_2 J m_J\rangle = -\,S_J|\pm;\, Jm_J\,|\Omega|=1/2\rangle + C_J|\pm;\, Jm_J\,|\Omega|=3/2\rangle \qquad (5.123)$$

where $$S_J = \left(\frac{X - 2 + Y}{2X}\right)^{\frac{1}{2}} \qquad (5.124)$$

$$C_J = \left(\frac{X + 2 - Y}{2X}\right)^{\frac{1}{2}} \qquad (5.125)$$

X and Y have been given already in equation (5.85). We therefore require the matrix elements

$$\begin{aligned}\langle\pm;\, F_2\, Jm_J|H_z|\pm;\, F_2 Jm_J\rangle = {} & S_J^2\langle\pm;\, Jm_J 1/2|H_z|\pm;\, Jm_J 1/2\rangle \\ & - 2C_J S_J\langle\pm;\, Jm_J 1/2|H_z|\pm;\, Jm_J 3/2\rangle \\ & + C_J^2\langle\pm;\, Jm_J 3/2|H_z|\pm;\, Jm_J 3/2\rangle \qquad (5.126)\end{aligned}$$

These matrix elements are diagonal in all quantum numbers and hence lead directly to the required eigenvalues. The relevant matrix elements of our Zeeman Hamiltonian are

$$\langle \pm;\ Jm_J 1/2 | H_z | \pm;\ Jm_J 1/2 \rangle$$

$$= \frac{\mu_B B_0 m_J}{2J(J+1)} \left\{ g_L - \tfrac{1}{2} g_S + 2g_r \left[\tfrac{1}{4} - J(J+1) \right] \mp \tfrac{1}{2}(g_l' + g_r^{e'})(2J+1) \right\} \tag{5.127}$$

$$\langle \pm;\ Jm_J 3/2 | H_z | \pm;\ Jm_J 3/2 \rangle$$

$$= \frac{\mu_B B_0 m_J}{2J(J+1)} \left\{ 3g_L + \frac{3}{2} g_S + 2g_r \left[\frac{9}{4} - J(J+1) \right] \right\} \tag{5.128}$$

$$\langle \pm;\ Jm_J 3/2 | H_z | \pm;\ Jm_J 1/2 \rangle$$

$$= \frac{\mu_B B_0 m_J}{2J(J+1)} \left\{ + g_S + g_L + g_r \pm g_r^{e'}\ (J + 1/2) \right\} \left[(J - 1/2)(J + 3/2) \right]^{\frac{1}{2}} \tag{5.129}$$

Substitution of these matrix elements into (5.126) together with expressions for S_J and C_J leads to

$$\begin{aligned} E = \frac{\mu_B B_0 m_J}{2J(J+1)} \Bigg\{ & g_L \left(\frac{2X - 2 + Y}{X} \right) + g_S \left(\frac{X - 4 + 2Y - 4(J - 1/2)(J + 3/2)}{2X} \right) \\ & + \tfrac{1}{2} g_r \left(\frac{5X - 8 + 4Y}{X} - 4J(J+1) - \frac{4(J - 1/2)(J + 3/2)}{X} \right) \\ & - g_l \; \frac{2(J - 1/2)(J + 3/2)}{X} \mp (g_l' + g_r^{e'})(J + 1/2) \left(\frac{X - 2 + Y}{2X} \right) \\ & \mp g_r^{e'}\ (J - 1/2)(J + 1/2)(J + 3/2) \frac{2}{X} \Bigg\} \end{aligned} \tag{5.130}$$

Comparison with (5.120) gives us the relationship between Radford's effective g-factors and our fundamental g-factors, for the $^2\Pi_{1/2}$ state of OH:

$$\begin{aligned} \bar{g}_J = \frac{1}{2J(J+1)} \Bigg\{ & g_L \left(\frac{2X - 2 + Y}{X} \right) + g_S \left(\frac{X - 4 + 2Y - 4(J - 1/2)(J + 3/2)}{2X} \right) \\ & - (g_r + g_l) \; \frac{2(J - 1/2)(J + 3/2)}{X} \\ & + \tfrac{1}{2} g_r \left(\frac{5X - 8 + 4Y - 4XJ(J+1)}{X} \right) \Bigg\} \end{aligned} \tag{5.131}$$

$$\Delta g_J = \frac{1}{J(J+1)}\Big\{- g_r^{e'}(J-1/2)(J+1/2)(J+3/2)\,\frac{2}{X} \\ - (g_l' + g_r^{e'})(J+1/2)\;\frac{X+2-Y}{2X}\Big)\Big\} \qquad (5.132)$$

As expected, therefore, the difference between $(\delta g_J)_L^+$ and $(\delta g_J)_L^-$ can be related to our Λ-doubling g-factors g_l' and $g_r^{e'}$.

5.8 Analysis of Measured Transition Frequencies

Eigenvalue calculations, predictions of spectra and least-squares fitting were performed on a CDC 7600 computer. Programmes written by Dr. F.D. Wayne to perform such calculations on $^3\Sigma$ and $^1\Delta$ states were available and so it was only necessary to modify these to obtain a programme applicable to $^2\Pi$ states. The main changes involved the replacement of those subrontines calculating matrix elements with ones relevant to our $^2\Pi$ effective Hamiltonian. The least-squares fitting procedure is based on that of Castellano and Bothner-By (37).

The basis sets used in the programme are the paritised basis functions defined in equation (5.9). This halves the sizes of the matrices and helps to reduce computing time.

In order to fit the Zeeman data it is first necessary to be able to calculate the zero-field transition frequencies accurately. The most extensive analysis of the zero-field data was performed by Meerts and Dymanus (14) who were able to fit most of the lines to within 25kHz. They also included six lines reported by Poynter and Beaudet (8) but could not fit these so well, the discrepancies varying from 65 to 940 kHz. It was hoped that we could take the parameters determined by Meerts and Dymanus, convert these to our parameters, as described in section 5.6, and hence to calculate the zero-field transition frequencies with an accuracy comparable to theirs, thus leaving us to concentrate on fitting the g-factors. The success of this comparison will be discussed in due course.

We shall first deal with the development and testing of our programme. Our initial version did not include centrifugal distortion and third-order hyperfine terms. Since Meerts and Dymanus included such terms in their fit we cannot in this instance hope to fit the data as accurately as them. However we can check that the usual Λ-doubling, rotational and hyperfine terms are correct. The terms in B and A can be checked fairly easily against standard matrix elements, e.g. Hougen (25). The hyperfine matrix elements were checked against those given by Carrington <u>et al</u> (38) for NS. The Λ-doubling matrix elements can be checked against those of Carrington and Lucas (35). A useful comparison can be made with the Λ-doubling expressions given by Dousmanis, Sanders and Townes (7). For this we have to set all but A, B, $\underline{q}$ and $\underline{(p + 2q)}$ to zero, and these latter parameters we take from the Meerts and Dymanus results:

$$\begin{aligned} A &= -139.38\text{cm}^{-1} = -4178507.865\text{MHz} \\ B &= 18.515\text{cm}^{-1} = 555065.814\text{MHz} \\ \underline{q} &= 2\alpha_7 = -1165.22\text{MHz} \\ \underline{(p + 2q)} &= 4\alpha_3 - 2\alpha_5 = 4737.628\text{MHz} \end{aligned} \qquad (5.133)$$

$\underline{q}$ and $\underline{p + 2q}$ are determined from equation (5.91) by setting the third order terms, D_p and D_q, to zero. The B parameter was not determined by MD since their data do not include transitions between rotational levels, so that B cannot be constrained in a least-squares fit. Instead they adopted the Dieke and Crosswhite value (6).

The Λ-doubling intervals computed with the above parameters are given in table 5. For comparison the experimentally determined Λ-doubling frequencies ν_Λ and those calculated from the DST expression given in (5.84) are also given. Discrepancies between the results of the DST calculation and the observed data probably arise from neglect of the higher order contributions, $\nu_\Lambda^{(2)}$, to the Λ-doubling frequencies. In our case discrepancies are probably due to neglect of centrifugal distortion corrections. The agreement between observed and calculated transition frequencies is therefore as good as can be expected, and our calculation compares satisfactorily with the DST expressions.

If the dominant hyperfine effects are included we can compare directly with the observed transition frequencies (those collected from various sources and tabulated by Meerts and Dymanus (14) have proved most convenient to use, since they span a wide range of rotational levels and on the whole are measured to a high degree of precision). Again, we use the hyperfine parameters determined by MD and convert them to our parameters using equations (5.39) and (5.40). We thus obtain

$$\begin{aligned} a &= 86.01\text{MHz} \\ \alpha' &= -74.04\text{MHz} \\ \beta'' &= 44.04\text{MHz} \\ d &= 56.62\text{MHz} \end{aligned} \qquad (5.134)$$

	J	Experimental	Our Calculation	DST Calculation
$^2\Pi_{3/2}$	3/2	1666.34[a]	1664.02	1664.347
	5/2	6036.596[a]	6042.218	6135.9519
	7/2	13437.8[a]	13507.681	
	9/2	23822.98[b]	24044.697	
	11/2	36989.41[b]	37507.07	
$^2\Pi_{1/2}$	1/2		4737.629	4737.629
	3/2	7797.59[c]	7799.984	7810.908
	5/2	8166.08[c]	8153.788	8169.513

a Taken from Radford (4)

b Taken from Dousmanis, Sanders and Townes (7)

c Taken from Radford (5)

Table 5 Λ-doubling intervals in absence of hyperfine and centrifugal distortion effects.

The hyperfine Λ-doubling frequencies calculated using the parameters given in (5.133) and (5.134) differ quite considerably from the observed transition frequencies. For instance, for the $^2\Pi_{3/2}$ states, those calculated for the J = 3/2 levels have discrepancies of about 2.6MHz while those for the J = 11/2 levels differ by 517.5MHz. These discrepancies were ascribed to our neglect of centrifugal distortion effects on the Λ-doubling and so further matrix elements (i.e. those in D_p and D_q) were incorporated in the programme to account for these.

At this stage the usual rotational centrifugal distortion terms in D_B were also included, although these are expected to give only very slight contributions to the Λ-doubling and certainly would not account for the discrepancies mentioned above. D_B affects the Λ-doubling intervals only indirectly, in that it alters the extent of spin-uncoupling in the molecule. $Y = \frac{A}{B}$ is a measure of the spin-uncoupling and D_B can be regarded as a J-dependent contribution to B:

$$B \cong B_0 - D_B J(J+1)$$

An estimate of this effect can be obtained from the DST expression (5.84). If we assume that there is no change in A and that D_B is 10^{-4}B then a calculation of ν_Λ using this modified value of Y reveals that for the $^2\Pi_{3/2}$ J = 3/2 levels the change in ν_Λ ought to be 0.5MHz. A computer calculation shows the corresponding change to be about 0.83MHz.

Values of D_B, D_p and D_q were taken from Meerts and Dymanus (14). Their D_B value is that of Dieke and Crosswhite (6) and is

$$D_B = 56.06 \text{ MHz} \qquad (5.135)$$

Matrix elements of D_B were checked against those of Zare (39), with appropriate changes in sign to allow for differences in phase convention. The D_p and D_q parameters were calculated using (5.91) and this entails alterations in the $\underline{q}$ and $\underline{p + 2q}$ parameters given in (5.133). Meerts and Dymanus quote

$$\alpha_3 = 1184.407 \text{ MHz}$$
$$\alpha_4 = -2.937 \text{ MHz}$$
$$\alpha_5 = 2.813 \text{ MHz}$$
$$\alpha_7 = -582.61 \text{ MHz}$$

We need an α_8 value before we can convert to our parameters and so we calculate this from α_5 using equation (5.92) and setting B = 16.961 cm^{-1} (Dieke and Crosswhite value). Hence α_8 = 0.2361 MHz, which leads to

$$\begin{aligned} \underline{p + 2q} &= 4732.4742 \text{ MHz} \\ \underline{q} &= -1164.3877 \text{ MHz} \\ D_p &= -0.7202 \text{ MHz} \\ D_q &= 0.4722 \text{ MHz} \end{aligned} \qquad (5.136)$$

Centrifugal distortion corrections to A were also included, although their effect on the spectra is very slight. As mentioned in section 5.5, we choose to incorporate these as a spin-rotation interaction (parameter γ) rather than as a term in A_J, since γ and A_J are highly correlated and it is only necessary to include one. In this case the parameter γ that we wish to use is a linear combination of the true γ and the A_J constants, the relationship being

$$\gamma_{\text{apparent}} = \gamma - \left(\frac{A - 2B}{B}\right) A_J \qquad (5.137)$$

A corresponding expression would hold were we to use A_J rather than γ. Neither a γ nor an A_J term was included by Meerts and Dymanus, and neither have been determined for OH by other workers. We must thus resort to some other means of estimating γ. Both γ and A_J have been determined for OD by Coxon (39) and so we can use an isotopic substitution method to obtain a value for γ in OH. Brown and Watson (28) have pointed out that the separation of and A_J by previous workers is based on an incorrect assumption and so a value of γ_{apparent} determined from Coxon's results might not be reliable. However, since the γ term is not very important for $^2\Pi$ states this is not expected to introduce serious errors. We have the relationships

$$\frac{\gamma\,(OD)}{\gamma\,(OH)} \simeq \frac{B\,(OD)}{B\,(OH)} \simeq \frac{A_J\,(OD)}{A_J\,(OH)} \qquad (5.138)$$

and so from Coxon's values of

$$\begin{aligned} \gamma\,(OD) &= 1.34 \times 10^{-3} \text{ cm}^{-1} \\ B\,(OD) &= 9.8831 \text{ cm}^{-1} \\ A_D\,(OD) &= 2A_J = -4.36 \times 10^{-4} \text{ cm}^{-1} \end{aligned}$$

we obtain for OH :-

$$\begin{aligned} \gamma &= 2.51 \times 10^{-3} \text{ cm}^{-1} \\ A_J &= -4.084 \times 10^{-4} \text{ cm}^{-1} \end{aligned}$$

Substitution into (5.137) gives the required value of γ :

$$\gamma_{\text{apparent}} = -1.3812 \times 10^{-3}\ \text{cm}^{-1}$$
$$= -41.4\ \text{MHz} \qquad (5.139)$$

The matrix elements of D_p and D_q are not easy to check since the Λ-doubling centrifugal distortion Hamiltonian has not been given in this form before. A rather useful, and rigorous, check on the Λ-doubling, centrifugal distortion and γ terms in the programme is possible in the case b) limit. This involves setting $A = 0$. The usual case b) expressions (1) for a molecule in a doublet state, in the absence of hyperfine effects, are of the form

$$F_1(N) = B[N(N+1) - \Lambda^2] - D_B[N(N+1) - \Lambda^2]^2 + \tfrac{1}{2}\underline{q}N(N+1) + \tfrac{1}{2}\gamma N$$
$$F_2(N) = B[N(N+1) - \Lambda^2] - D_B[N(N+1) - \Lambda^2]^2 - \tfrac{1}{2}\underline{q}N(N+1) - \tfrac{1}{2}\gamma(N+1)$$
$$(5.140)$$

Our D_p and D_q terms arise from cross terms of the rotational and usual Λ-doubling Hamiltonians. In the case b) limit therefore we expect a term in D_q of the form

$$\pm \tfrac{1}{2} D_q\, N(N+1)\,[N(N+1) - \Lambda^2] \qquad (5.141)$$

where the upper and lower signs refer to F_1 and F_2 levels respectively.

To test our programme in the case b) limit we have to set $A = 0$, $\underline{p + 2q} = \underline{2q}$ and, by analogy with the p + 2q term, $D_p = 2D_q$. The eigenvalues calculated in this way are found to be the same as those given by (5.140) and (5.141), except for the γ terms, which are in error by $-\tfrac{1}{2}\gamma$. This is because the spin-rotation interaction should be of the form

$$H_{SR} = \gamma\, \underline{R}.\underline{S} = \gamma(\underline{N} - \underline{L}).\underline{S} \qquad (5.142)$$

whereas the terms in γ in (5.140) are eigenvalues of the $\gamma\underline{N}.\underline{S}$ part only. A contribution of the form $-\gamma\langle L_z S_z\rangle = -\tfrac{1}{2}\gamma$ should therefore be included in (5.140), so it is the case b) expressions that are in error rather than our programme. Herzberg (1) quotes the case b) expressions only for the particular case of $^2\Sigma$ states, in which case the form of (5.140) is indeed correct.

The fit of the Λ-doubling frequencies using the values of the centrifugal distortion parameters obtained above is still not as good as that obtained by Meerts and Dymanus. The $^2\Pi_{3/2}$ J = 3/2 levels now have a discrepancy of 4.6 MHz and the J = 11/2 levels have deviations of 437.2 MHz. This is no better than the fit without centrifugal distortion terms. The only difference between this present programme and that of Meerts and Dymanus is that we have not at this stage included the third-order hyperfine terms and they have not included a γ term. These are not expected to be particularly large and would not account for the above discrepancies - the γ term, for instance, gives a shift of only 66 kHz to the $^2\Pi_{3/2}$ $J = 3/2$ Λ-doubling frequencies, and the contribution from the hyperfine Λ-doubling d_{β}' term is not expected to be very much larger. If both Meerts and Dymanus's results and our programme are reliable then we ought to be able to calculate the zero-field frequencies to a reasonable degree of accuracy. With the exception of the D_p and D_q terms all our matrix elements have been checked against ones previously published and even the D_p, D_q terms give satisfactory results in the case b) limit. It is possible that an error exists in the MD least-squares fitting routine, which would explain our inability to fit the data with their parameters. In view of this it was decided to attempt to fit the zero-field data ourselves. The B, A and hyperfine constants were fixed at the MD values given in (5.133) and (5.134). This programme had no provision for varying the hyperfine parameters. The remaining parameters were allowed to vary in the least-squares fit. We used the data set tabulated by MD, with a weighting inversely proportional to the variance of the individual lines (standard deviations on each of the lines were also quoted by MD).

We found that γ was very poorly constrained, with a large standard deviation, which is to be expected since the transition frequencies have only a weak dependence on γ. An initial fit gave a value of

$$\gamma = 396.14 \text{ MHz} \quad (\sigma = 1439.1)$$

and so in a second fit γ was fixed at this value. The values for the remaining parameters thus obtained were

$$\begin{aligned}
\underline{q} &= -1168.635 \text{ MHz} \ (\sigma = 0.082) \\
\underline{p+2q} &= 4732.504 \text{ MHz} \ (\sigma = 0.130) \\
D_p &= -0.6592 \text{ MHz} \ (\sigma = 0.0132) \\
D_q &= 0.4329 \text{ MHz} \ (\sigma = 0.0119) \\
D_B &= 144.101 \text{ MHz} \ (\sigma = 6.217)
\end{aligned} \qquad (5.143)$$

With the exception of the D_B term, these parameters do not differ much from their initial values. The large change in D_B is not to be viewed with alarm. In a similar fit on OH Destombes <u>et al</u> (41) obtained a value for D_B of 106.66 MHz. That this differs from ours as well as the Dieke and Crosswhite value is probably not significant - they have included only one Λ-doubling parameter as opposed to our four, so their fit will converge to different values of the constants to compensate for this. All that concerns us with their results is that their D_B value is much larger than that of Dieke and Crosswhite so the latter is not to be regarded as immutable.

The transition frequencies calculated with the set of parameters given in (5.143) fit the observed data very well, and in some instances the fit is even better than that of Meerts and Dymanus. Column I in table 6 shows the deviations from the observed frequencies. For the $^2\Pi_{3/2}$ J = 3/2 levels the frequencies are calculated to within 5 to 16kHz, whereas MD fitted these to within 28kHz. Similarly, the $^2\Pi_{3/2}$ J = 11/2 levels we fit to within 150 kHz, in contrast to 920kHz by MD.

A comparison with Meerts and Dymanus's results is rather difficult since the assignments they present in their paper are ambiguous. They use a Wang basis set rather than a parity basis set and so our $\pm$ labels are not necessarily the same as theirs. Furthermore, it is not clear from their data which of their F quantum numbers labels the lower state. In order to obtain our assignments we had to examine carefully the zero-field eigenvalues for each of the m_F-blocks from $m_F = 0.0$ to $m_F = 6.0$. This range of m_F-blocks allows us to assign unambiguously all the F labels for both $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ levels with J = 1/2 up to J = 11/2. This procedure led to the important observations that the parity labels are inverted for $^2\Pi_{1/2}$ states with $J \geqslant 9/2$, and the F labels are inverted for $^2\Pi_{3/2}$ states with $J \geqslant 7/2$ - for each of the other J levels the higher of the F labels refers to the state with the higher energy.

In our case the discrepancies show a general increase with J, which seems to indicate the need for further higher order corrections. The programme used for the above fit does not include λ^3 hyperfine terms and as has already been mentioned has no provision for fitting any hyperfine parameters. A further version of the programme was developed to remedy these omissions, and this was rather more successful.

We first fitted only the λ^2 hyperfine, Λ-doubling and centrifugal distortion terms, using initial values taken from the data in (5.134) and (5.143). The resulting fit is, on the whole, very much better than the previous one, and the discrepancies from the observed data are shown in column II of table 6. Only for the $^2\Pi_{3/2}$ J = 3/2, 7/2 and 11/2 levels do we achieve a better fit than Meerts and Dymanus. Our best fit is for the $^2\Pi_{3/2}$ J = 3/2 levels, which we calculate to within 0.3 to 14kHz. Most of the remaining lines can only be calculated to within 20 to 970kHz. The deviations do not show a particularly marked dependence on J. The parameters obtained from the above fit are as follows:

$$\underline{q} = -1168.673\text{MHz} \ (\sigma = 0.064)$$

$$\underline{p+2q} = 4732.476\text{MHz} \ (\sigma = 0.102)$$

Table 6 Observed and calculated zero-field transition frequencies for OH

Ω	J	Parity (lower)	F upper	F lower	Observed Frequency (MHz)	Frequency differences (obs-calc) (in kHz)			
						I	II	III	Meerts & Dymanus
3/2	3/2	+	1	1	1665.4018(2)	-14.7	-14.4	-61.6	26.0
			2	2	1667.3590(2)	15.7	14.3	42.7	27.4
			2	1	1720.5300(2)	-4.99	0.393	-9.52	25.4
			1	2	1612.2310(2)	6.18	-0.329	-9.30	28.0
	5/2	-	2	2	6030.747(5)	-40.4	3.74	-99.5	-20.2
			3	3	6035.092(5)	22.1	62.8	137	-18.2
			3	2	6049.084(8)	-539	-334	-25.3	-21.7
			2	3	6016.746(5)	511	392	53.4	-25.7
	7/2	+	3	3	13434.62(1)	13.7	11.0	-154	-65
			4	4	13441.36(1)	56.8	51.9	181	-100
	9/2	-	4	4	23817.615(2)	-32.5	-35.6	-266	6.3
			5	5	23826.621(3)	58.0	51.9	240	5.5
			4	5	23838.46(1)	347	342	-400	-480
			5	4	23805.13(1)	-968	-972	-272	-150
	11/2	+	5	5	36983.47(3)	-149	-146	-441	-910
			6	6	36994.43(5)	-39.7	-40.3	209	-940
1/2	1/2	-	1	1	4750.656(3)	-71.2	-59.7	26.5	27.5
			1	0	4765.562(3)	-511	-27.9	-122	19.3
			0	1	4660.242(3)	388	-39.8	-118	24.7
	3/2	+	1	1	7761.747(5)	-3.03	48.1	-77.4	-7.5
			2	2	7820.125(5)	-119	-92.5	-17.4	0.3
			2	1	7831.962(5)	-16.4	32.2	-40.5	1.1
			1	2	7749.909(5)	107	-77.6	-55.3	-9.2

5/2	-	2	2	8135.870(5)	151	165	112	0.8
		3	3	8189.587(5)	-112	-121	83.8	4.6
		3	2	8207.402(5)	228	79.3	22	5.8
		2	3	8118.051(5)	-194	-39.5	2.51	-4.5
7/2	+	3	3	5473.045(5)	293	300	317	-4.3
		4	4	5523.438(5)	-98.7	-177	-191	-12.6
		4	3	5547.042(5)	95.6	93.9	69.1	-9.1
		3	4	5449.436(5)	25.8	24.2	52.2	-12.8
9/2	+	5	5	117.1495(10)	338	336	407	-5.6
		4	4	164.7960(10)	-319	-341	-426	-4.1
		5	4	192.9957(10)	305	-17.5	-8.85	-11.3
		4	5	88.9504(10)	-286	13.5	-9.85	2.1
Weighted sum of squares of deviations in $(\mathrm{MHz})^2$					0.0203	0.0107	0.0216	

Observed frequencies quoted by Meerts and Dymanus (14) (see references cited therein for workers responsible for individual measurements)

Numbers in brackets after observed frequencies are standard deviations, and apply to the last significant figure of the frequency

I Fit of Λ-doubling and centrifugal distortion terms
II As for I but including λ^2 hyperfine terms
III As for II but including λ^3 hyperfine terms

$$
\begin{aligned}
D_p &= -0.6506\text{MHz } (\sigma = 0.0104) \\
D_q &= 0.4289\text{MHz } (\sigma = 0.0094) \\
D_B &= 146.061\text{MHz } (\sigma = 4.883) \\
a &= 85.777\text{MHz } (\sigma = 0.150) \\
\alpha' &= -72.947\text{MHz } (\sigma = 0.130) \\
\beta'' &= 43.270\text{MHz } (\sigma = 0.159) \\
d &= 56.669\text{MHz } (\sigma = 0.452)
\end{aligned}
\qquad (5.144)
$$

None of these values are significantly different from the initial data. The standard deviations on the first five terms are lower than those from the previous fit given in (5.143).

We next attempted to reduce some of the discrepancies in the above fit by including the λ^3 hyperfine terms, and fitting these in conjunction with the λ^2 hyperfine parameters. The centrifugal distortion and Λ-doubling constants were fixed at the values given in (5.144). The d_a constant was not fitted, for reasons already mentioned, and was fixed at zero. We were not able to obtain a value for D , since it is strongly correlated with C_I, a and α'. Meerts and Dymanus had the same difficulty, as mentioned in section 5.6. This term too was fixed at zero. The values obtained for the remaining hyperfine terms are as follows:

$$
\begin{aligned}
a &= 86.078\text{MHz } (\sigma = 0.370) \\
\alpha' &= -73.592\text{MHz } (\sigma = 0.696) \\
\beta'' &= 43.748\text{MHz } (\sigma = 0.546) \\
d &= 56.519\text{MHz } (\sigma = 0.648) \\
C_I &= -0.089\text{MHz } (\sigma = 0.093) \\
d_{\beta'} &= 0.306\text{MHz } (\sigma = 0.203)
\end{aligned}
\qquad (5.145)
$$

The value of C_I is very similar to that of 0.1MHz which we can obtain from Meerts and Dymanus's results using (5.97). Note that the standard deviations on the four λ^2 terms are larger than those given in (5.144). Indeed the fit using this data set is not as good as that in the absence of λ^3 hyperfine terms. The deviations from the observed transition frequencies are shown in column III of table 6. There seems to be no trend in the deviations with respect to J which might indicate that the remaining errors are merely experimental, but considering the precision to which the lines are determined, and the magnitude of the discrepancies, a more likely explanation is that higher order terms other than the λ^3 hyperfine terms need to be included.

We now turn to a fit of the Zeeman data. E.p.r. studies have been made on the following rotational levels: $^2\Pi_{3/2}$ J = 3/2 through to J = 11/2; $^2\Pi_{1/2}$ J = 3/2 and 5/2. It is our intention to use all these measurements in our fit. The measurements of the $^2\Pi_{3/2}$ J = 9/2 lines were detailed in section 5.4. The J = 11/2 lines have been measured in this laboratory by Dr. C.L.M. Kerr while the remaining lines were measured by Radford (4, 5). The frequencies and field positions of the latter lines are not given in Radford's papers and so it was decided to regenerate this data by substitution of the given parameters into Radford's transition frequency expressions. A computer programme was written by Dr. M. Kaise for this purpose. At this stage Dr. Radford provided us with the original data for all his measurements, and so this was used in preference to any computed data. It is worth pointing out, however, that although the aforementioned programme gave predictions for the $^2\Pi_{3/2}$ data to within 0.2 to 1.6 gauss we were not able to regenerate the $^2\Pi_{1/2}$ data satisfactorily. Although the average field position and overall spread of the lines was correct, the relative dispositions and assignments of individual lines were totally different. The calculation of the $^2\Pi_{1/2}$ data entails only a minor correction to the expressions for the $^2\Pi_{3/2}$ levels which according to Radford adds only about 1.5MHz to the transition energies. For the J = 3/2 levels, which have an effective g-factor of -0.134, this means a shift in field positions due to this additional term of about 8 gauss. If we omit this correction term we have essentially a $^2\Pi_{3/2}$ programme which from the above is known to be correct and so we should at least be able to predict the $^2\Pi_{1/2}$ lines to within 8 gauss. This course of action does not, however, lead to any improvement. This would seem to indicate that there are errors in Radford's $^2\Pi_{1/2}$ effective parameters.

The weighting for the Zeeman lines was based on the inverse squares of the linewidths, which is similar to that adopted for the zero-field lines. Radford quotes linewidths of 450kHz for the strongest lines (presumably the $^2\Pi_{3/2}$ J = 3/2 levels), 800kHz for the weaker $^2\Pi_{3/2}$ lines and 2MHz for the $^2\Pi_{1/2}$ measurements. For our J = 9/2 measurements the linewidths are estimated to be about 10 gauss for the resolved lines and 20 gauss for the unresolved ones. For the J = 11/2 lines the linewidths were estimated to be

20 gauss. Since the least-squares programme fits frequencies and not fields it is first necessary to convert the linewidths for the J = 9/2 and 11/2 lines to frequencies. This entails calculating the effective g-factors for these levels, since Radford does not quote them. These are best calculated from the expressions relating the effective g-factors, $\bar{g}_J$, for F_1 levels to the molecular g-factors g_S, g_L etc. In this approximate calculation only the dominant contributions, those from g_S and g_L, need be included. The expression for F_2 levels was given earlier in section 5.4. That for F_1 levels is similar and for our purposes we can take this to be

$$\bar{g}_J = \frac{1}{2J(J+1)}\left[g_L\left(\frac{2X+2-Y}{X}\right) + g_S\left(\frac{X+4-Y+4(J-1/2)(J+3/2)}{2X}\right)\right] \tag{5.146}$$

We thus obtain g_J values of 0.138 and 0.197 for the J = 9/2 and 11/2 levels respectively, which lead to frequency linewidths of 5.52MHz for the J = 11/2 levels, and 1.94 and 3.87MHz for resolved and unresolved J = 9/2 levels respectively. The simple case a) expressions for effective g-factors

$$\bar{g}_J = \frac{(g_S\Sigma + g_L\Lambda)}{2J(J+1)}$$

was found to give g-factors an order of magnitude smaller than the above and so it is necessary to use the intermediate coupling scheme expression given in (5.146).

The linewidths and resulting weights used in the initial fit are therefore as follows:

Ω	J	$\Delta\nu$(MHz)	Weight
3/2	3/2	0.45	1
	5/2	0.80	0.3164
	7/2	0.80	0.3164
	9/2	1.94 res.	0.054
		3.87 unres.	0.0135
	11/2	5.52	0.00665
1/2	3/2	2.0	0.0506
	5/2	2.0	0.0506

The zero-field parameters used were those obtained from the best fit of the zero-field data and are those given in (5.144) together with the A and

B values given in (5.133). g_N was fixed at the value of 5.585, obtained from Radford's g_I value of -3.042×10^{-3}. The remaining g-factors were allowed to vary in the least squares fit. The resulting fit is very disappointing - the lines could only be calculated to within 10 - 60MHz and the g-factors were also not very well determined. The values obtained were:

$$g_S = 2.0133 \ (\sigma = 0.1392)$$

$$g_L = 0.9923 \ (\sigma = 0.0789)$$

$$g_r = 0.0022 \ (\sigma = 0.0073)$$

$$g_l = -0.0295 \ (\sigma = 0.2309)$$

$$g_r^{e'} = 0.0021 \ (\sigma = 0.0008)$$

$$g_l' = 0.0043 \ (\sigma = 0.0136)$$

g_S and g_L we would expect to be slightly less than their free electron values of 2.00232 and 1.000 respectively and so g_S is certainly too large. g_l' and $g_r^{e'}$ are of the order that we would expect but both g_r and g_l are an order of magnitude too large; these should be about 10^{-4} and 10^{-3} respectively. Note also that these two g-factors have very large standard deviations which indicates that they are not very well constrained by the data. In addition the least squares programme indicates that g_r is highly correlated with g_L and g_l with g_S. In a second fit both g_r and g_l were constrained to be zero and the data fitted to the remaining four g-factors. This improved the fit slightly - the lines could be calculated to within 0.2 to 25MHz but this is still not satisfactory. The g-factors are somewhat better determined in this case, the values being

$$\begin{aligned} g_S &= 2.0111 \ (\sigma = 0.0015) \\ g_L &= 0.9981 \ (\sigma = 0.0010) \\ g_r^{e'} &= 0.0020 \ (\sigma = 0.0001) \\ g_l' &= 0.0043 \ (\sigma = 0.0009) \end{aligned} \qquad (5.148)$$

The Λ-doubling g-factors $g_r^{e'}$ and g_l' have the same values as in (5.147) and so these were fixed at the above values in subsequent runs. In these we fixed g_r either at zero or at Radford's value for g_N' (which is equivalent to our g_r) of 3.7×10^{-4}, and allowed g_S, g_L and g_l to vary. The best fit was obtained from the latter, although this is far from satisfactory. The

$^2\Pi_{3/2}$ J = 3/2 lines could be fitted to within 33 to 700kHz but the lines from higher rotational levels could not be fitted as well as this. By far the worst fit was for the $^2\Pi_{3/2}$ J = 11/2 lines which had mean residuals of about 40MHz. Table 7 shows the results of this fit. Data from one set of the J = 9/2 and one set of the J = 11/2 measurements are omitted, since these are very similar to the ones tabulated. Two sets of $^2\Pi_{3/2}$ J = 3/2 measurements were used, since these spectra are the most accurately determined of all the measurements. The g-factors obtained from this fit are

$$g_S = 1.9855 \ (\sigma = 0.0018)$$

$$g_L = 1.0079 \ (\sigma = 0.0008)$$

$$g_l = 0.0372 \ (\sigma = 0.0024)$$

The differences between these values and those given in (5.147) and (5.148) are quite marked - g_S is now far too small; g_L we would expect to be slightly less than unity; g_l, admittedly better constrained, has changed sign and is still an order of magnitude too large.

5.9 Discussion

In this section we shall try to draw conclusions from the results presented in the previous section. We shall deal first with the zero-field problem.

It is unfortunate that we had to spend so much time on obtaining an adequate description of the zero-field energy levels, since it is the g-factors that we are really interested in. It was hoped that we could have used the Meerts and Dymanus results directly, which proved not to be possible, and we certainly did not anticipate that we would have to perform our own analysis of the zero-field data. Even though we had to resort to this course of action we still were not able to reproduce Meerts and Dymanus's results, and there are several possible explanations for this. First, since we are not certain as to what assignments MD have used, we could be using a different set of assignments to them. Secondly, there appears to be errors in their least-squares fitting procedure. As mentioned in section 5.6, their α_5 parameter can be rewritten as a contribution to the α_3 and α_4 constants and so it is not at all clear how they managed to determine α_3, α_4 and α_5 simultaneously. Fitting these three terms should not have given a convergent fit. Their apparently good fit is therefore to be viewed with some suspicion and so we should not be perturbed at the inferior quality of our fit.

Table 7 Observed and calculated Zeeman measurements for OH

Ω	J	m_F value for parity		Observed		Obs − calc Frequency
		+	−	Frequency (MHz)	Field (gauss)	(MHz)
3/2	3/2[a]	1.0	2.0	9262.93	5787.69	0.477
		0.0	1.0	"	5790.68	0.512
		−1.0	0.0	"	5793.42	0.672
		0.0	1.0	9263.00	5809.63	−0.185
		−1.0	0.0	"	5811.93	−0.157
		−2.0	−1.0	"	5813.93	0.033
		2.0	1.0	9259.92	8301.71	−0.576
		1.0	0.0	9260.12	8321.53	−0.434
		1.0	0.0	9259.92	8334.19	−0.255
		0.0	−1.0	9260.12	8354.84	−0.143
		0.0	−1.0	9259.98	8367.15	0.043
		−1.0	−2.0	9259.95	8388.65	0.119
		1.0	2.0	8902.26	5512.98	0.284
		0.0	1.0	"	5515.43	0.236
		−1.0	0.0	"	5517.45	0.568
		0.0	1.0	8902.21	5534.15	0.524
		−1.0	0.0	"	5535.93	0.428
		−2.0	−1.0	"	5537.32	0.632
		2.0	1.0	8902.26	8030.45	−0.718
		1.0	0.0	"	8050.29	−0.712
		1.0	0.0	"	8061.29	−0.564
		0.0	−1.0	"	8081.29	−0.485
		0.0	−1.0	"	8092.25	−0.057
		−1.0	−2.0	"	8114.09	−0.404
3/2	5/2[a]	−1.0	−2.0	9470.77	5022.03	0.519
		−2.0	−3.0	"	5025.97	0.588
		0.0	−1.0	"	5039.27	0.459
		−1.0	−2.0	"	5045.42	0.422
		1.0	0.0	"	5056.44	0.434
		0.0	−1.0	"	5064.54	0.464

		2.0	1.0	"	5073.49	0.475
		1.0	0.0	"	5083.56	0.555
		3.0	2.0	"	5090.85	0.291
		2.0	1.0	"	5102.64	0.583
3/2	7/2[a]	3.0	2.0	9277.59	8922.67	-1.05
		4.0	3.0	"	8935.36	-1.20
		2.0	1.0	9277.67	8988.48	-1.45
		3.0	2.0	"	8998.46	-1.22
		1.0	0.0	9278.35	9055.39	-1.51
		2.0	1.0	"	9061.67	-1.33
		0.0	-1.0	9277.07	9128.57	-1.48
		1.0	0.0	"	9131.41	-1.16
		0.0	-1.0	9277.58	9199.10	-0.947
		-1.0	-2.0	"	"	-1.72
		-1.0	-2.0	9278.31	9267.03	-1.21
		-2.0	-3.0	"	9272.47	-1.31
		-2.0	-3.0	9278.29	9339.31	-1.12
		-3.0	-4.0	"	9348.74	-1.27
3/2	9/2[b]	-4.0	-5.0	26253.16	6821.90	2.50
		-3.0	-4.0	26253.22	6852.46	1.97
		-3.0	-4.0	26253.35	6882.82	2.27
		-2.0	-3.0	26253.93	6909.37	1.92
		-2.0	-3.0	26254.26	6945.78	2.20
		-1.0	-2.0	26254.51	6966.29	1.89
		-1.0	-2.0	26258.32	7025.50	-3.64
		0.0	-1.0	26258.32	7025.50	4.44
		0.0	-1.0	26262.10	7096.52	0.152
		1.0	0.0	26262.10	7096.52	3.05
		1.0	0.0	26262.58	7155.67	1.32
		2.0	1.0	26262.58	7155.67	2.60
		3.0	2.0	26262.67	7215.47	1.66
		2.0	1.0	26262.67	7215.47	2.11
		4.0	3.0	26262.79	7275.35	0.842
		3.0	2.0	26262.79	7275.35	3.00
		5.0	4.0	26253.14	7335.08	-9.60
		4.0	3.0	26253.14	7335.08	-5.74

3/2	11/2[c]	5.0	4.0	35459.000	5203.2	8.45
		4.0	3.0	"	5348.7	32.1
		6.0	5.0	"	5367.6	43.9
		3.0	2.0	"	5408.3	29.9
		5.0	4.0	"	5436.1	46.2
		2.0	1.0	"	5469.9	27.7
		4.0	3.0	"	5506.9	48.6
		3.0	2.0	"	5536.1	38.6
		1.0	0.0	"	5579.0	38.3
		2.0	1.0	"	5601.0	38.3
		0.0	-1.0	"	5652.4	38.1
		1.0	0.0	"	5667.0	37.8
		-1.0	-2.0	"	5728.6	38.0
		0.0	-1.0	"	5737.8	38.0
		-2.0	-3.0	"	5806.7	37.7
		-1.0	-2.0	"	5810.4	38.1
		-2.0	-3.0	"	5885.3	38.1
		-3.0	-4.0	"	5888.4	37.7
		-3.0	-4.0	"	5961.4	37.8
		-4.0	-5.0	"	5974.4	38.1
		-4.0	-5.0	"	6041.2	37.7
		-5.0	-6.0	"	6062.3	38.2
1/2	3/2[d]	-1.0	-2.0	9200.055	7316.68	1.68
		0.0	-1.0	"	7429.42	1.68
		2.0	1.0	"	7484.26	1.46
		1.0	0.0	"	7535.23	2.34
		1.0	0.0	"	7535.23	0.704
		0.0	-1.0	"	7578.68	1.67
	5/2[d]	2.0	3.0	9200.01	5129.01	-7.53
		-3.0	-2.0	"	5148.93	-7.56
		-2.0	-1.0	"	5175.14	-7.46
		-1.0	0.0	"	5198.26	-7.19
		1.0	2.0	"	5198.26	-8.16
		0.0	1.0	"	5222.92	-7.65
		1.0	2.0	"	5244.01	-7.78
		0.0	1.0	"	5265.41	-8.02
		-1.0	0.0	"	5335.75	-8.13
		-2.0	-1.0	"	5407.55	-8.14

a Lines measured by Radford (4)
b Present measurements
c Lines measured by Dr. C.M.L. Kerr
d Lines measured by Radford (5)

Weighted Sum of squares of deviations of fit = 443.054 (MHz)^2

Our analysis has indicated that the terms in our effective Hamiltonian are not quite sufficient to describe the rotational energy levels. Inclusion of the λ^3 hyperfine terms gives no significant improvement, and it is likely that alternative higher order terms are required. These could be further centrifugal distortion corrections to the rotational constant, H_v and so on, or, more likely, fourth order Λ-doubling interactions. We have not had time to investigate either of these possibilities.

The fourth order Λ-doubling terms would be of the form

$$(\lambda^2 H_{LD})(H_{ROT})^2$$

As for the third order terms we would expect the vibrational contributions to be more important than the electronic ones. A cursory glance reveals that there are in principle six such parameters:

2 involving $\langle v = 0|H_{LD}|v' \neq v\rangle$

2 involving $\langle v = 0|H_{LD}|v = 0\rangle$

2 involving $\langle v' \neq v|H_{LD}|v' \neq v\rangle$

However, some of these would be either linear combinations of others, or of equivalent form to a lower order Λ-doubling term. Hence less than six parameters would be determinable. As before, only Σ states would be expected to contribute to these parameters, to fourth order.

For the sake of completeness, we present in table 8 the best set of zero-field parameters obtained from our analysis. For comparison the corresponding parameters obtained from Meerts and Dymanus's work are included also.

The analysis of the Zeeman measurements has not proceeded as well as we would have liked. Our extremely poor fit indicates that there are still some problems to be resolved and we certainly cannot rule out the possibility of a programming error, even though all the matrix elements have been checked. It is not clear why the residuals should be so large - these could not be accounted for by the discrepancies remaining in the zero-field problem since the latter are minute, by comparison. Nevertheless, we can take the best set of g-factors that we have obtained so far and attempt to relate them to Radford's results. In addition, the two Λ-doubling g-factors, g_l' and $g_r^{e'}$ are quite well determined and so we can use these to obtain estimates of the molecular matrix elements, $\langle\Pi|T^1_q(\underline{L})|\eta'\rangle$ and so on, for comparison with a pure precession model. The 'best' set of g-factors is given in table 9.

Table 8 Best set of zero-field parameters, in MHz

	Our results	Standard deviation	Meerts & Dymanus
B	555065.814[a]	—	555065.814[a]
D_B	146.061	4.833	56.06[a]
A	-4178507.865[b]	—	-4178507.865
q	-1168.673	0.064	-1164.3877
$p+2q$	4732.476	0.102	4732.4742
D_p	-0.6506	0.0104	-0.7202
D_q	0.4289	0.0094	0.4722
γ	396.64	1439.1	—
a	85.777	0.150	86.01
α'	-72.947	0.130	-74.04
β''	43.270	0.159	44.04
d	56.669	0.452	56.62
subsequent run:			
C_I	-0.089	0.093	0.1
$d_{\beta'}$	0.306	0.203	—
d_a	—	—	—
$D_{\beta'}$	—	—	—

a Dieke and Crosswhite value (6)

b Meerts and Dymanus value (14)

Table 9 Molecular g-factors obtained from best fit

		Standard Deviation
g_S	1.9855	0.0018
g_L	1.0079	0.0008
g_r	0.00037	—
g_N	5.585	—
g_l	0.0372	0.0024
$g_r^{e'}$	0.0020	0.0001
g_l'	0.0063	0.0008

The pure precession model applies to systems of spherical symmetry. A simple picture of OH views this molecule as a large oxygen atom with a small hydrogen atom orbiting around it, and so this system has near spherical symmetry. It would thus be expected to conform closely to the pure precession model. The pure precession hypothesis assumes that $\underline{L}^2$ is a constant of motion and so L is well defined. For L = 1 the only excited states that are present are those with L = 0. Therefore the only excited states that contribute to our general perturbation expressions for $^2\Pi$ effective parameters are $^2\Sigma$ states. This greatly simplifies those expressions, leading to:

$$\underline{q} = -4(\Delta E)^{-1}|\langle\Pi_{+1}|BT^1_1(\underline{L})|\Sigma\rangle|^2$$

$$\underline{p+2q} = 4(\Delta E)^{-1}\langle\Pi_{+1}|(A + 2B)\ T^1_1(\underline{L})|\Sigma\rangle\langle\Sigma|BT^1_{-1}(\underline{L})|\Pi_{+1}\rangle$$

$$g'_l = 2g_L(\Delta E)^{-1}\langle\Pi_{+1}|AT^1_1(\underline{L})|\Sigma\rangle\langle\Sigma|T^1_{-1}(\underline{L})|\Pi_{+1}\rangle$$

$$g^{e'}_r = -4g_L(\Delta E)^{-1}\langle\Pi_{+1}|BT^1_1(\underline{L})|\Sigma\rangle\langle\Sigma|T^1_{-1}(\underline{L})|\Pi_{+1}\rangle$$

$$g_l = \tfrac{1}{2}g'_l$$

$$g^e_r = \tfrac{1}{2}g^{e'}_r$$

$$\Delta g_L = -g^e_r \qquad (5.150)$$

where $\Delta E = (E_\Sigma - E_\Pi)$ and Δg_L is a correction to g_L due to the admixture of excited electronic states. This term has been defined by Brown and Uehara (42).

It is not immediately apparent how the relations given in (5.150) are obtained from the general perturbation expressions. Certain factors of $\frac{1}{2}$ and (-1) appear as a result of substitution of explicit values for q. In addition the general expressions should strictly be written in Hermitian average form, as given by Carrington and Lucas (35), and this has been taken into account in the derivation of (5.150).

Taking the best values of $\underline{q}$ and $\underline{p+2q}$ from table 8, the molecular matrix elements involved in the expressions for these can be computed. This requires a value for ΔE and from ultra violet work this is known to be 32682.5 cm^{-1}. The resulting matrix elements, $\langle\Pi|BT^1_1(\underline{L})|\Sigma\rangle$ and

$\langle \Pi | AT_1^1(\underline{L}) | \Sigma \rangle$, are given in table 10. The value of the former is in close agreement with that calculated by Radford, the latter was not determined in his papers. Note that to relate Radford's results to ours we have to multiply his by $\sqrt{2}$ since he uses L_y, rather than $T_1^1(\underline{L})$, operators. Substitution of these results into $g_r^{e'}$ or g_l' respectively yields estimates for $\langle \Sigma | T_{-1}^1(\underline{L}) | \Pi \rangle$. In the case of pure precession this element would have the value of 1.0. Using $g_r^{e'}$ we obtain a value of 0.9156, while from g_l' we obtain 0.9536. Our determinations of $g_r^{e'}$ and g_l' are therefore consistent with both Radford's results and those obtained using a pure precession model. The difference between our two estimates might be a reflection of the importance of third order contributions to $\underline{q}$ and $\underline{p+2q}$, which we have ignored in this model.

Since $g_r^{e'}$ and g_l' appear to be well determined it would be instructive to determine the sizes of the remaining g-factors using the relations given in (5.150). Thus:

$$g_l = 0.00315$$

$$g_r^e = -\Delta g_L = 0.001$$

Thus a g_r value of

$$g_r = g_r^N - g_r^e = -0.000458$$

would be expected. Note that the electronic contribution apparently outweighs the nuclear in this case.

The g_S and g_L values have to be corrected for relativistic effects, and these corrections are of the form $-g_S \langle T \rangle / mc^2$ and $-g_L \langle T \rangle / mc^2$ respectively, where $\langle T \rangle$ is the mean kinetic energy of a π electron. Assuming this electron to be localised on the oxygen atom, Radford (4) obtains $\langle T \rangle = 1.3 \times 10^{-4} mc^2$. The corrections to g_S and g_L are therefore -0.0002603 and -0.00013 respectively. The g_L term has further to be corrected for the effects of admixture of $^2\Sigma$ states:

$$(g_L)_{obs} = g_L + \Delta g_L$$

The expected values for g_S and g_L are thus

$$g_S = 2.00206$$

$$g_L = 0.99887$$

If we compare the g-factors given in table 9 with those determined above we

	Our result	Radford (5)
$\langle \Pi \| BT^1_1(\underline{L}) \| \Sigma \rangle$	-53.504×10^4 MHz	-53.671×10^4 MHz
$\langle \Pi \| AT^1_1(\underline{L}) \| \Sigma \rangle$	323.6723×10^4 MHz	—
$\langle \Sigma \| \underline{T}^1_1(\underline{L}) \| \Pi \rangle$	$\begin{cases} 0.9156 \\ 0.9536 \end{cases}$	0.9482

Table 10 Molecular matrix elements in a pure precession case

see that there are gross differences: the experimental values of g_S and g_L are particularly unsatisfactory, the former being much too small and the latter too large. g_l is an order of magnitude greater than anticipated and g_r is of the opposite sign (implying that the <u>nuclear</u> contributions are dominant, not the electronic ones).

Since Radford's $\bar{g}_J$ expressions are related to these four erroneous molecular g-factors it would be useful to calculate the $\bar{g}_J$ from our results for comparison. For the $^2\Pi_{1/2}$ levels we use the F_2 expressions given in (5.131) and (5.132), while for the $^2\Pi_{3/2}$ levels the corresponding F_1 expressions (36) have to be used. The resulting effective parameters are given in table 11. In view of the dubious values of g_S, g_L, g_l and g_r the agreement between our calculated $\bar{g}_J$ values and those of Radford is surprisingly good. The values of Δg_J calculated from $g_r^{e'}$ and g_l' are seemingly in poor agreement with Radford's observed values which is surprising since $g_r^{e'}$ and g_l' were previously found to be consistent with Radford's results. However, it must be pointed out that these two g-factors appear in second order of perturbation theory and would be expected to be very sensitive to the admixture of excited states. A calculation has been performed (43) to determine relations for $\bar{g}_J$ and Δg_J using more exact forms for S_J and C_J than those given in (5.124) and (5.125). These take into account the Λ-doubling contributions to the zero-field energies and lead to a revised form for Δg_J:

$$\Delta g_J' = \Delta g_J + \frac{2(J - 1/2)(J + 1/2)(J + 3/2)(Y + 1)}{BJ(J + 1)X^3}\left[(\underline{p+2q}) + (Y - 2)\underline{q}\right] \qquad (5.151)$$

for F_1 levels. A corresponding expression for F_2 levels has not been derived. The calculated values of $\Delta g_J'$ are given in table 11 and are seen to be in very close agreement with Radford's Δg_J values. Thus, our values of $g_r^{e'}$ and g_l' and indeed consistent with Radford's results. By comparison the dominant contributions to $\bar{g}_J$ (from g_L and g_S) are not expected to be particularly sensitive to higher order contributions and so the form for $\bar{g}_J$ given in (5.131) is sufficient.

It is not clear why the molecular g-factors in table 9 should give such good determinations of $\bar{g}_J$. It is possible that there is not a unique set of g-factors, g_S, g_L, g_r, g_l, giving the required $\bar{g}_J$ values, and our least-squares programme has converged to a different combination than expected. Alternatively there could be an error in one or more of these Zeeman matrix elements. In an attempt to obtain more reasonable molecular

Table 11 Effective g-factors calculated from the molecular g-factors

		Calculated			Radford's measurements*	
Ω	J	$\bar{g}_J$	Δg_J	$\Delta g'_J$	$\bar{g}_J$	Δg_J
3/2	3/2	0.9357	−0.0007	−0.00128	0.93557	−0.00129
	5/2	0.4856	−0.00109	−0.001855	0.48529	−0.00188
	7/2	0.32583	−0.001363	−0.00214	0.32561	−0.00214
1/2	3/2	−0.13394	−0.001593		−0.13393	−0.00099
	5/2	−0.14245	−0.001018		−0.14113	0.00042

$$\Delta g_J = g_J^+ - g_J^-$$

$\Delta g'_J$ are Δg_J values calculated using exact zero-field coefficients

* $^2\Pi_{3/2}$ measurements from reference (4)

$^2\Pi_{1/2}$ measurements from reference (5) g-factors we have tried to fit the data using the g_S value of 2.00206 obtained earlier. g_r was constrained to be zero. Values of

$$g_L = 1.00136 \ (\sigma = 0.00033)$$

$$\text{and} \quad g_l = 0.01231 \ (\sigma = 0.00139)$$

were obtained, which, although an improvement on the ones in table 9, are still unsatisfactory. The quality of the fit was marginally worse than that of the preceding one.

The analysis of the Zeeman data is still incomplete and there is obviously considerable room for improvement.

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CHAPTER 6

RADICAL PRODUCTION BY PYROLYSIS

6.1 Introduction

This chapter describes some preliminary work concerned with the use of pyrolysis to generate radicals, and their subsequent detection by gas phase e.p.r. spectroscopy.

The most commonly used methods of radical production for gas phase e.p.r. studies rely on the use of a microwave discharge. The radicals are either produced directly by the discharge or by subsequent mixing of the discharge products with a second gas, as in the case of OH, described in the previous chapter. The discharge methods have proved reasonably successful, so one might inquire as to what advantages the pyrolysis technique offers over them. One obvious advantage is that there is no discharge noise to contend with. Secondly, the concentrations of relevant radicals in the discharge products is very low, of the order of 1-2% at best, whereas if suitably high temperatures are reached the relative concentration of radicals emerging from a furnace can be very high, in certain instances as much as 100%. Finally there is the possibility of detecting radicals hitherto undetectable by other means. For instance, the radicals CH_3 and CN, which have long eluded detection by gas phase e.p.r., are quite readily generated by pyrolysis of diazomethane (1) and cyanogen (2) respectively. However, the use of pyrolysis in e.p.r. studies has remained largely uninvestigated, although certain molecules, with low dissociation energies, have been studied.

A case in point is the pyrolysis of tetrafluorohydrazine, N_2F_4, to produce the radical species NF_2

$$N_2F_4 \rightleftharpoons NF_2 \qquad (6.1)$$

At temperatures of around 500-600°C the N_2F_4 is almost 100% dissociated. The NF_2 spectrum is readily detected by e.p.r. spectroscopy but because of the multitude of observable lines there is a considerable problem in assignment. Little information has been obtained so far from an e.p.r. study of NF_2 as only the surface of the problem has been scratched. However, Brown, Burden, Godfrey and Gillard (3) have performed an extensive analysis of the NF_2 rotational levels by use of ordinary microwave spectroscopy.

The pyrolysis of N_2F_4 has been utilised in order to generate NF radicals (4) by the admixture of the products of a microwave discharge in hydrogen.

$$NF_2 + H \longrightarrow NF + HF \qquad (6.2)$$

NF has been detected by gas phase e.p.r. in its $^1\Delta$ state by Curran, Macdonald, Stone and Thrush (5).

A hot-wire technique has also been used in e.p.r. studies to produce such radicals as halogen atoms (6, 7) and OH, SO and SH (8). In this case, however, the radicals are not produced solely by the action of heat as the wire itself has an important catalytic effect.

In the field of mass spectrometry, pyrolysis has been used to generate radicals since the early 1940's. An extensive list of these radicals detected by mass spectrometry has been given by Lossing (9). Similarly, pyrolysis has found much use in photoelectron spectroscopy - radicals such as CH_3 (1, 10), NF (11), SO (12) and S_2 (13), for example, have been detected in this manner.

The reason pyrolysis has not been used so extensively in e.p.r. studies is due essentially to practical difficulties. Firstly, the e.p.r. method involves the use of a resonant cavity and, as has been discussed in chapter 4, the resonant frequency of such a cavity depends critically on its dimensions. There is bound to be a certain amount of heat transfer to the cavity body and so the resonant frequency will tend to drift during the course of the experiment. Since the detection system relies on the frequency of the microwave source being more or less identical to that of the cavity, the effect will be to cause instability in the system. This will manifest itself as a poor signal-to-noise ratio, base-line drift, or, in an extreme case, as an inability to keep the source frequency locked to that of the cavity. Random cooling of the cavity by draughts also tends to cause variations in the base-line.

Secondly, there is the matter of furnace efficiency. Previous investigations of the use of pyrolysis in this laboratory have involved heating a fairly large area of the glass inlet tube by enclosing it within a long electrically heated furnace. Because of the large areas of glass through which heat can be conducted it is not possible to achieve very high temperatures. The inlet tube is of fairly large cross-section (say 2 cm diameter) and so any gas flowing through it is not very efficiently heated. In addition, since the glass is connected to the cavity body this provides a direct route for heat transfer to the cavity. However, the success of the small furnaces used by Lossing (9, 14) seems to indicate that a small region of intense heat can result in efficient radical production. The present experiments involve the use of such a small furnace, situated at the tip of a small quartz probe, and will be described in more detail in the next section. It is sufficient to point out at this stage that because of the small cross-section of the probe, and because of the small amount of glass involved, high temperatures can be reached and efficient transfer of heat to the gas is possible. Heat transfer to the cavity is minimal since the probe is not directly connected to the cavity body.

Unfortunately, this experiment did not get much further than the drawing board, but we present here, for future reference, details of the construction of the furnace and of some preliminary tests. The instigation to do this work was provided by Dr H.Kroto of Sussex University, with whom this is a joint project.

Various radicals are proposed for future study. The CH_3 and CN radicals mentioned earlier are perhaps a little ambitious. The CN radical requires temperatures of at least 1700°C (2) which in our case is prohibitively high. The transitions in CH_3 are mainly magnetic dipole allowed and hence will be very weak. The bending vibrational mode in CH_3 will result in an oscillating electric dipole but since this will be very small the electric dipole transitions are also expected to be very weak. Radicals perhaps more amenable to study are CH_3S, CH_3O and C_6H_5S. The former has been detected in the pyrolysis products of dimethyldisulphide (15) at temperatures of 500-900°C. The pyrolysis to form C_6H_5S occurs at even lower temperatures (around 200°C) but this is not really a suitable molecule to study since its rotational partition function is so large. CH_3O has recently been detected by Radford (16) using laser magnetic resonance, the method of preparation being the abstraction of a hydrogen atom from methanol by fluorine atoms. An alternative preparation is via the pyrolysis of dimethyl peroxide, which occurs at temperatures of around 100°C. CH_3O and CH_3S are prolate symmetric top molecules, the K doublets for each rotational level being degenerate for $|K| > 0$. We would expect to see $\Delta m_J = \pm 1$ electric dipole transitions between these two K components, within a rotational state. C_6H_5S is a near symmetric top molecule and so the K degeneracy will be lifted, but for the lower rotational levels this splitting will be small and possibly will not be resolvable in an X-band experiment. The g-factor in the higher rotational levels will be very small and so it will not be possible to tune these lines into resonance in an X-band e.p.r. study.

A point of interest concerning CH_3O and CH_3S is that it might be possible to determine the extent to which the electronic orbital angular momentum is quenched by the internal rotation of the methyl group. This would give information on how much of the orbital angular momentum is localised on the oxygen (or sulphur) atom, and to what extent it is quantised along the C-O (or C-S) bond. In addition these molecules would exhibit a Jahn-Teller phenomenon and information on this would be interesting.

6.2 Some Initial Experiments

The prototype furnace was provided by Dr H. Kroto and is of similar design to that of Lossing and Tickner (14). The furnace itself is cut from a piece of tantalum foil of 0.050 mm thickness and the design is shown in figure 1. This is formed into a cylindrical shape by wrapping it around a former of suitable circumference, the resulting shape being shown in figure 2. The tags on the end of this furnace are for the electrical contacts. Figure 2 shows that the furnace can be regarded as two coils, each of one turn only, connected in series such that the magnetic fields induced in the coils cancel out. This is to avoid any interaction with the Zeeman modulation field which could lead to mechanical instability.

The tantalum furnace is sited at the tip of a quartz glass probe, which is constructed from two concentric glass tubes. The inner tube is about 18" long and of 0.15" outer diameter; it is through this tube that the sample gas is to be passed. The outer tube is merely to keep the furnace in position around the inner one, and is of the length of the furnace. These two tubes are joined at their ends. The internal diameter of the outer tube and the external diameter of the inner one have to be carefully chosen so that the furnace will slide between them.

The resonant cavity is of the 'wide access' type discussed in chapter 4, and operates in a TE_{012} mode. Since the cavity has to be evacuated for studies of gaseous samples, a cylindrical quartz pillbox is placed inside it. This has gas ports at each end, which protrude through holes in the flat ends of the cavity body, and is constructed so as to fit snugly to the internal walls of the cavity. This does not disturb the resonant modes unduly - there is a shift in frequency of about 35 MHz for the TE_{012} mode and a slight decrease in the Q-factor (to about 6000). With the pillbox in place the resonant frequency is about 8690 MHz.

The probe is situated inside the gas inlet tube, such that the tip lies just at the edge of the cavity. There is some difficulty in incorporating the probe into the vacuum system and in passing electric current through the furnace. This problem was resolved by Dr Kroto, who provided us with a brass cone assembly which would fit a standard glass B29 socket. With this end in mind, the gas inlet tube of the quartz pillbox is fitted with such a socket. The thin probe tube passes through a hole in the centre of the cone assembly. An O-ring provides a vacuum seal and also helps to hold the probe in position. Adjustment of the position of the probe tip is possible using this system. A short length of plastic tubing connects the probe tube to a gas handling line.

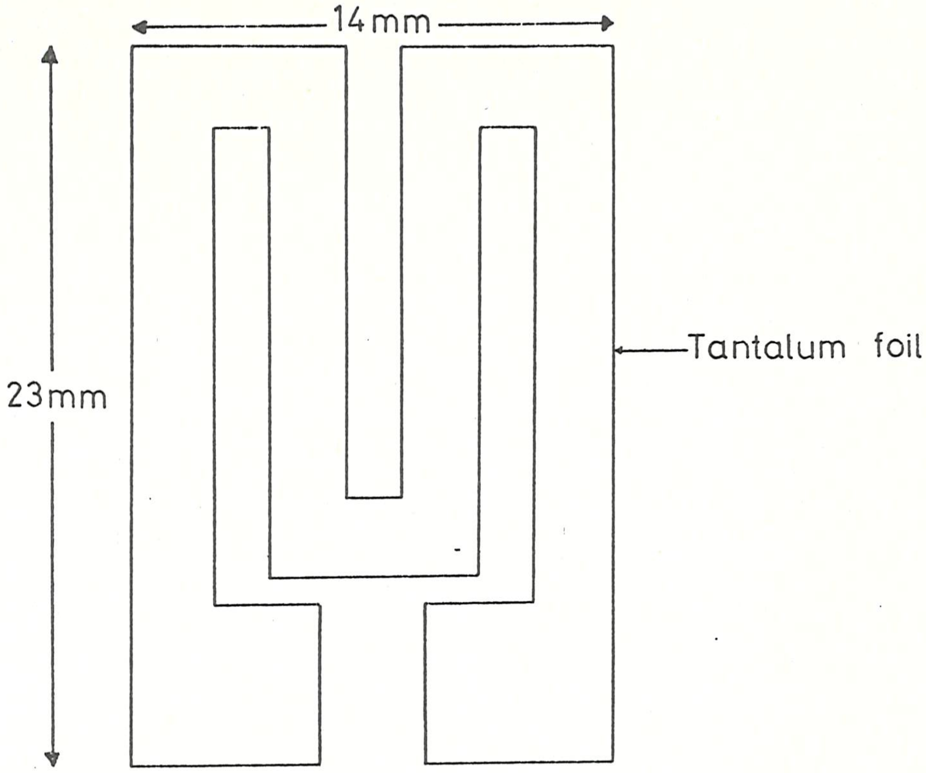


Figure 1 Furnace element as cut from metal foil.

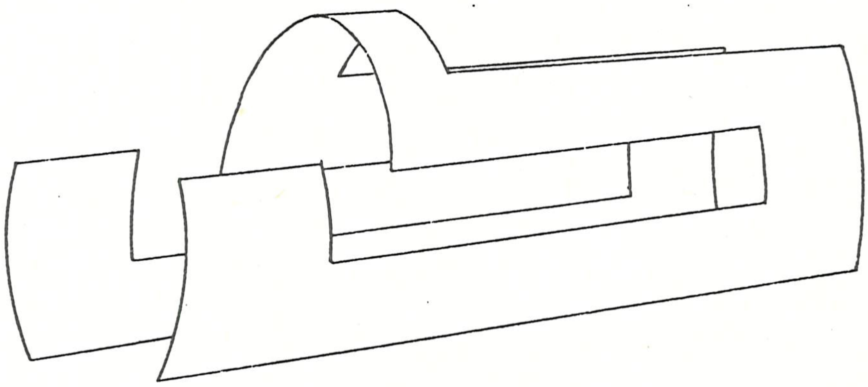


Figure 2 Furnace element in cylindrical form.

The metal cone assembly is provided with four electrical feed-throughs, two for the furnace and two for a thermocouple. The tantalum furnace is connected to the feed-throughs by two lengths of thin copper rod. Stainless steel tips are soldered to on end of these rods and the tags of the furnace are spot-welded to these. The other end of the copper rods are soft-soldered to the feed-throughs. A chromel-alumel thermocouple is used and is bound to the outside of the probe tip with asbestos string. Figure 3 shows a cross-section through the quartz pillbox, with the probe in place.

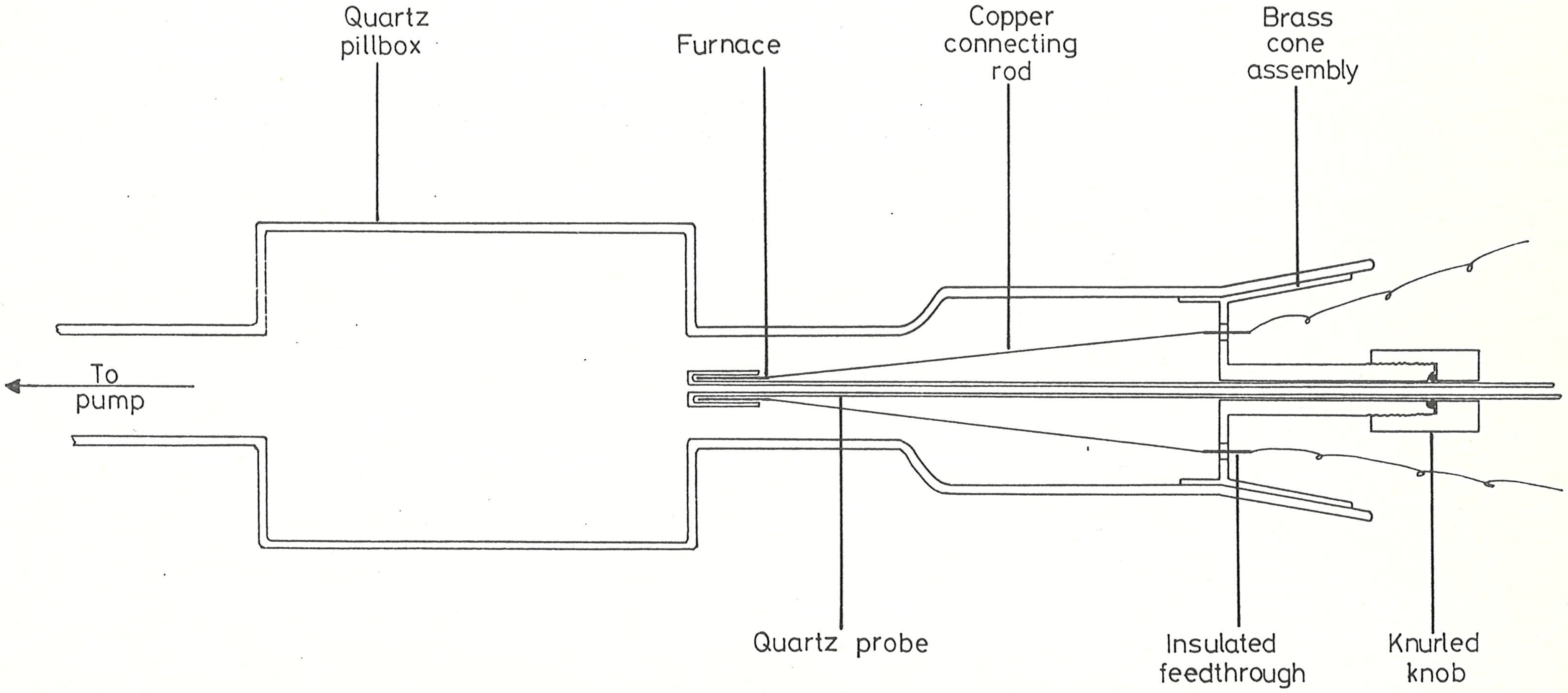
The spectrometer system consists of a standard X3 e.p.r. spectrometer with a Varian 12-inch electromagnet and Fieldial regulating system. The spectrometer operates at 8670 MHz, so it is necessary to shift the resonant frequency of the cavity to this frequency. This can be achieved by inserting small pieces of Teflon into the cavity, or by adjusting the position of the pillbox slightly so as to vary the quantity of quartz that disturbs the resonant modes. The power supply for the furnace is a Roband Varex twin DC power supply capable of delivering up to 30 volts and 10 amps, either voltage- or current-regulated. We tried both but have found that only voltage-regulation is satisfactory - the temperature of the furnace can increase uncontrollably when using current-regulation.

The furnace was tested initially without any sample gas. Great care must be taken to ensure that a short circuit in the furnace does not occur. Contact of the 'coils' can occur in one of two ways, first, through movement of the probe tube, which tends to cause torsion in the furnace, and secondly, through expansion of the tantalum on heating. To counteract this, it was found necessary to reduce the dimensions of the furnace slightly, and in particular its overall width. Paradoxically, it was found better to decrease the width of the gaps between the tantalum. If the widths of the tantalum strips are reduced the furnace loses mechanical strength and it is extremely difficult to insert it into the concentric probe without twisting it. The problem of of twisting is avoided by using wider strips of tantalum with smaller gaps between them. Furthermore, if short, fine strands of quartz are placed in the gaps as spacers, shorting out can be avoided altogether.

A further difficulty encountered was that the furnace tended to burn out if the temperature was increased too rapidly. This was avoided by raising or lowering the temperature by incremental amounts.

Table 1 shows the results of a test run on the furnace. The temperatures indicated by the thermocouple are considerably lower than expected on comparison with a colour scale of temperature. For instance, incipient red heat corresponds to $\sim 500^\circ$C on a colour scale whereas the thermocouple indicates 190°C. Similarly, incipient white heat should correspond to $\sim 1500^\circ$C while

Figure 3



Cross-section through cavity and furnace assembly

V(volts)	I(amps)	T(°C)	Observations
1.0	2.8	54	
2.3	5.8	190	Incipient red heat
3.0	6.3	256	Red heat
3.5	6.4	290	
4.0	7.6	365	
5.0	9.0	420	
6.0	10.0	510	Yellowish-white heat
7.0	9.4	550	Burns out Incipient white heat

Temperatures obtained using chromel-alumel thermocouple.

Table 1 Sample results from test run on tantalum furnace.

the thermocouple reads only 550°C. It was noticed that the asbestos string tended to harden and expand at high temperatures, pulling the thermocouple away from the surface of the probe in the process, and this most likely accounts for the discrepancy in the temperatures. Further experiments are needed to determine the furnace temperatures reliably.

Tests were also performed to check the spectrometer sensitivity. Spectra of molecular oxygen and NO (produced from a microwave discharge in air) were recorded with signal-to -noise ratios of about 100 to 1 and 20 to 1 respectively. The S:N ratio for NO prepared in this way is comparable to that normally obtained at X-band using the alternative type of microwave cavity. As a more rigorous test we also searched for magnetic dipole transitions in NO_2. At pressures of about 1.7 torr a broad triplet was observed at around $g_S = 2$, as one would expect. On reduction of the pressure, smaller peaks were observed but only as far as about 3800 gauss, beyond this they were too weak to be seen. These higher field lines are predicted to be extremely weak so it does not necessarily follow that the spectrometer lacks sensitivity. The above tests on stable frre radicals indicate that the sensitivity is satisfactory, though far from excellent.

Brief searches were made for the unstable radicals OH and SH, by pyrolysis of H_2O and H_2S respectively. Our failure to observe OH is not surprising in view of the strength of the O-H bond. The SH experiments stand more chance of success, but no spectra could be observed, even though the furnace was taken to almost white heat. Tests on radicals produced at lower temperatures are needed, but as yet none have been made.

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